PB-222 627

FEASIBILITY OF PLASTIC FOAM PLUGS FOR SEALING LEAKING CHEMICAL CONTAINERS

R. C. Mitchell, et al

Rockwell International Corporation

Prepared for:

Environmental Protection Agency

May 1973

DISTRIBUTED BY:

NTIS

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EPA-R2-73-251
MAY 1973

W73.13019

PB 222 627

Environmental Protection Technology Series

Feasibility of Plastic Foam Plugs for Sealing Leaking Chemical Containers

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SELECTED WATER RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

1. Report No.

2. Accession No. W 73-13019

4. Title: Feasibility of Plastic Foam Plugs for Sealing Leaking Chemical Containers, (all caps)

5. Report Date

6.

8. Performing Organization Report No.

Author(s): Mitchell, R. C., Hamermesh, C. L., Lecce, J. V. ~~Kirsch, M. and Siner, J. E.~~

10. Project No. Project EPA 15090 HGW

Organization: Rocketdyne Division of Rockwell International Corp~~oration~~ Canoga Park, California.

11. Contract/Grant No. ~~EPA~~ 68-01-0106

13. Type of Report and Period Covered

12. Sponsoring Organization

Environmental Protection Agency report ~~number~~, Technology Series EPA-R2-73-251, May 1973. 60p, 22 fig, 3 tab, 4 ref

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The feasibility of this concept was demonstrated. As a consequence of the success already realized, it is probable that a practical and useful system, embodying this approach, can be developed. ~~(Mitchell - Rocketdyne)~~ (EPA)

17a. Descriptors: *Water Pollution Control, *Sealants, *Chemicals, *Leakage, *Accidents, *Transportation, Plastics,

Copy available from GPO Sup Doc as EP 1.23/2:, $0.85 ; microfiche from NTIS as PB 222 627, ~~$0.95~~. 1.45

17b. Identifiers: ~~*Plugging Chemical Leaks~~, *Hazardous Chemicals Spills, ~~*Prevention of Water Pollution~~ *Chemical container leaks, *Plastic foam plugs

17c. COWRR Field & Group: 05G 08G

18. ~~Security Class.~~ (Report)

19. No. of Pages: 21

Send To: WATER RESOURCES SCIENTIFIC INFORMATION CENTER U.S. DEPARTMENT OF THE INTERIOR WASHINGTON, D. C. 20240

20. Security Class. (Page)

22. Price

Abstractor: R. C. Mitchell

Institution: Rocketdyne Division of Rockwell International Corporation

EPA-R2-73-251
May 1973

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Contract 68-01-0106

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OFFICE OF RESEARCH AND MONITORING

U. S. ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D. C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
Price 85 cents domestic postpaid or 60 cents GPO Bookstore

EPA Review Notice

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ABSTRACT

A program was conducted to evaluate the feasibility of methods for plugging leaks in damaged chemical containers by application of suitable plastic barriers. Such a system would be valuable in helping to prevent water pollution from spilled hazardous chemicals.

A large number of candidate sealants were evaluated in laboratory screening tests, including various urethane foams; polystyrene and polyvinyl acetate instant foams; filled and unfilled epoxy systems; and polysulfide, butyl, neoprene, and silicone rubber systems. The most promising results were obtained with the urethane foams. Additional evaluation and scaleup tests were made, including sealing of leaks of many different hazardous chemicals, application to leaks both under water and in air, and sealing of leaks in 55-gallon containers.

The feasibility of this concept was demonstrated. As a consequence of the success already realized, it is probable that a practical and useful system, embodying this approach, can be developed.

This report was submitted by the Rocketdyne Division of Rockwell International in fulfillment of Project Number 15090 HGW, Contract 68-01-0106, under the sponsorship of the Environmental Protection Agency. Work was completed in August 1972.

This report has been given the Rocketdyne Internal Report Number R-9054.

CONTENTS

		Page
Abstract		iii
Sections		
I	Conclusions and Recommendations	1
II	Introduction	3
III	Screening and Evaluation Tests	5
	Selection of Sealants	5
	Testing	6
IV	Scaleup Tests and Feasibility Demonstration	11
V	Preliminary Design and Development	27
	Envelope of Practical Applications	27
	Survey of Available Application Hardware	30
	Preliminary Development Tests	32
	Chemicals Which can be Sealed	37
	Preliminary Design Concepts	40
VI	Acknowledgements	47
VII	References	49
VIII	Publications and Patents	51
IX	Glossary	53
Appendix		
Derivation of Equations for Envelope of Practical Applications		55

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FIGURES

1.	Laboratory Mixing/Delivery System for Potential Sealants	12
2.	Simple Applicator With Foam	14
3.	Sealing a 1-1/2-Inch Hole	15
4.	Completed Seals	16
5.	Improved Applicator	17
6.	Preparing to Seal a 3-Inch Hole	18
7.	Moving the Applicator Into Position	19
8.	With Plunger in Place, Foam is Extruded Into the 3-Inch Hole	20
9.	When Leak Has Been Stopped, Applicator is Extracted	21
10.	3-Inch Hole Securely Sealed With Foam	22
11.	Foam Plug Formation Viewed From Inside Chemical Container	23
12.	Ruggedness of Foam Plug	24
13.	Benzene Leak Sealing Under Water	25
14.	Envelope of Practical Applications for Sealing Leaks in Nonsubmerged Containers	29
15.	Pressurize Foam Cylinders With Rocketdyne Mixing Gun	35
16.	Pressurizable Foam Cylinders, Mixing Gun, and Polyethylene-Lined Plunger-In-Cylinder Applicator	35
17.	Use of Mixing Gun to Supply Foam to Cylinder Applicator	36
18.	Foam-Filled Balloon Concept	41
19.	Hollow Rubber Cone Concept	42
20.	Moving Applicator Concepts	43
21.	Foam Cocoon Concept for Leaking Valves and Open Pipes	43
22.	Sketch of Basic Container in Different Attitudes	55

TABLES

1. Potential Sealants Screened 7
2. Hazardous Chemicals Tested and Small-Scale Sealing Test Results 8
3. Probable Leak Sealing Success With 100 Hazardous Chemicals 38

SECTION I

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. There is a vital need for systems that can prevent dispersion of a hazardous chemical. It is far better and easier to prevent a hazardous chemical from entering a waterway than it is to attempt to remove it after entry.

2. The feasibility has been demonstrated of a concept to help prevent dispersion of leaking hazardous chemicals by application of a suitable plastic barrier (e.g., plastic foamed in place) to a leaking chemical container to plug, seal, or enclose openings such as those from cracks, ruptures, open seams, and damaged valves.

3. There are a number of potential sealants that might be considered for use in a leak-plugging system (e.g., various types of polyurethane foams, polystyrene foams, polyvinyl acetate foams, epoxy systems, and rubber systems). Of those tested, the most promising are the urethane foams.

4. Urethane foams can be used to seal leaks of a large variety of chemicals such as methanol, insecticides, benzene, and styrene.

5. The potential of this leak-sealing concept is great enough to justify its development for operational use. It is probable that a practical and useful system embodying this concept can be developed

RECOMMENDATIONS

1. It is recommended that a prototype of an operational system be developed and demonstrated embodying the use of urethane foams applied in place to plug leaking chemical containers (considering a broad range of leaks, e.g., cracks, ruptures, open seams, damaged valves, etc.).

2. It is recommended that a careful evaluation be made to assess whether it is necessary and practical to attempt development of special sealants and techniques for sealing leaks of particularly difficult chemicals that cannot be satisfactorily sealed with urethane foams (e.g., strong acids).

SECTION II

INTRODUCTION

In a highly industrialized society, tremendous quantities of chemicals are produced and shipped to other sites for various uses. Many of these chemicals are quite hazardous when introduced into natural waters. The likelihood of accidental release to watercourses is increased by the many operations involved in the production, transfer, shipping, unloading, and ultimate utilization of the chemicals. Thus, it is not at all surprising that spills do occur.

Spills can occur in a variety of ways. For example, the most dramatic and generally most serious type occurs when a container is violently ruptured (sometimes accompanied by fire or explosion) and large quantities of the hazardous material are spilled almost instantaneously. A less catastrophic spill results when the container maintains its integrity, but suffers enough damage to cause leakage of the hazardous material at a moderate rate. The leaking chemical can enter the watercourse either directly (for example, as the result of a barge accident or a land-based container falling into the water) or by flowing or being washed into a drainage channel or percolating into the ground water supply.

Countermeasures that neutralize or treat hazardous chemicals that are already mixed and in the waterway may require hours or days to be initiated and involve the very difficult problem of handling large volumes of water. Therefore, there is a vital need for a system that can prevent further dispersion of the hazardous chemical by stopping the leak, regardless of whether the leaking container is on land or under water. The program described herein was directed toward this need, with the underlying philosophy that it is far better and easier to prevent a hazardous chemical from entering a waterway than it is to try to remove it after entry.

The goal of the program was to demonstrate the feasibility of a concept for plugging leaks of hazardous materials. The concept involves application of suitable plastic barriers (e.g., plastic foamed in place) to a leaking chemical container to plug, seal, or enclose cracks, ruptures, open seams, damaged valves, etc. The major tasks involved: (1) screening tests to determine the suitability of various currently available plastics (used in the broad sense to include rubbers, foamed systems, etc., in addition to polymer systems more normally considered as "plastics") as sealants for selected hazardous chemicals, such as methanol, insecticides, benzene, and styrene; (2) evaluation of parameters involved in sealing leaks with selected sealant/hazardous chemicals; (3) demonstration at about the 10-gallon level of the feasibility of this concept; and (4) preliminary work toward design and development of an operational system.

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SECTION III

SCREENING AND EVALUATION TESTS

SELECTION OF SEALANTS

The objective of this phase of the program was to screen and evaluate, on the laboratory scale, the utility of a wide variety of materials as potential sealants for leaks from chemical containers. Several criteria were selected for evaluating the sealants, including:

1. Sealants should develop sufficient strength and adhesion to a painted metal container to completely seal a leak.
2. The setting time of the sealants should be short.
3. Sealants should fill a hole completely, regardless of the irregularity of the opening.
4. Sealants should have satisfactory chemical resistance to important hazardous chemicals such as benzene, phenol, methanol, and insecticides.

The sealants tested can be divided into two groups: expanding and non-expanding types.

The expanding sealants included various types of foam systems such as Instant Foams (Monsanto Corporation, St. Louis, Missouri) and urethane foams [Nagle Corporation, Chicago, Illinois; MSA Corporation, Pittsburgh, Pennsylvania; Expanded Rubber and Plastics Corporation, Torrance, California (Stafoam); and Olin Corporation, New Haven, Connecticut (Autofroth)]. These materials have desirable attributes for this application in that the foams will conform to an irregularly shaped hole and the expansion of the foam should result in a tighter seal. This approach assumes that the foam ingredients are applied either before expansion occurs or while it is occurring. Thus, the normal extent of shrinkage which accompanies curing is not likely to result in the foam pulling away from the holes. Should shrinkage be so large that some leaks remain, a second application of foam to these few sites could correct the problem.

Foaming occurs as the result of expansion of trapped gas. The gas may be generated by a chemical reaction such as that of an isocyanate and water to produce carbon dioxide or by the decomposition of a blowing agent, such as N,N'-dimethyl N,N'-dinitrosoterephthalamide (Nitrosan, DuPont Corporation, Wilmington, Delaware). In some foams, volume increase is due to a physical process in which a low-boiling chemical which was dissolved in the formulation at higher pressures vaporizes when the formulation is released from a container at ambient pressures. Some foams employ both mechanisms for volume increase. The foam systems screened in this program included ones employing each mechanism and others with the combination.

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An equally important consideration is whether a foam system undergoes a chemical reaction during the expansion, resulting in a crosslinked product. Crosslinking is an advantage for such foams in that a crosslinked material is considerably more resistant to chemical attack than the corresponding uncrosslinked polymer. A shortcoming of crosslinked systems is that the chemical leaking from the container may inhibit or retard the crosslinking reaction, and thus decrease or destroy the utility of the foam.

The nonexpanding sealants examined included materials that reacted to achieve crosslinked structures as well as systems that were thermoplstic and served merely as mechanical seals. Various epoxy systems (both filled and unfilled), quick-curing silicone rubbers, and catalyzed polysulfide rubbers are examples of the former. Swollen neoprene, butyl rubber, and uncatalyzed polysulfide rubbers are all of the thermoplastic nonexpanding type.

TESTING

Initial screening tests were made using 8-ounce cylindrical paint cans as the containers for the leaking liquids. The cylindrical cans were painted with baked alkyl resin enamel (yellow drum paint, Techniform Laboratories, Venice, California). This enamel is used to paint the outside surface of chemical drums. Adhesion to an unpainted metal surface is generally greater than to a low-surface-energy painted surface. The worst case of adhesion is that of a greasy or dirty surface. However, this condition is difficult to reproduce; therefore, painted metal surfaces were used as a standard low-energy test surface. Sealants that were effective in plugging leaks because of their adherence to the outside of the containers could, therefore, be screened on these small cans with assurance that their adhesion behavior on large-scale containers would be similar. Holes of various sizes from about 1/8- to 3/4-inch diameter were punched near the bottom of the can, and the test hazardous chemical was poured into the can, while covering the hole temporarily, to prevent leakage while filling the can. At the start of the test, the cover over the hole was removed and the sealant candidate was applied using a spatula or spraying foam directly from its dispenser as rapidly as possible while the chemical was flowing through the hole. This procedure was employed for tests both in air or under water.

Table 1 lists the materials screened as potential sealants and their performance in plugging small-diameter, low-head leaks of either benzene or methanol, primarily in tests as described in the previous paragraph. As a result of these early successes, testing was expanded to include most of the hazardous chemicals that are ranked among the top 20 in the priority list (Ref. 1 and 2). In Table 2, these chemicals are listed as well as the degree of success obtained using various sealants (primarily polyurethane foams or epoxy resins) to seal holes in painted containers. Most of these tests were made with 1/4- to 3/4-inch holes in 8-ounce containers. It should be noted that even with these off-the-shelf unoptimized sealants, successful plugging of leaks of most of these chemicals

TABLE 1. POTENTIAL SEALANTS SCREENED

Type of Material	Source	Indication of Results
Polystyrene Instant Foam	Monsanto	Very rapid foaming; no adhesion to metal; may be suitable for mechanical seal
Modified (rubbery) Polystyrene Instant Foam	Monsantao	Very rapid foaming; no adhesion to metal; may be suitable for mechanical seal
Polyvinyl Acetate Instant Foam	Monsanto	Very rapid foaming; no adhesion to metal; may be suitable for mechanical seal
Urethane Foam	Nalge	Aerosol-type cans give inadequate mixing and delivery; setting time probably too long to be useful*
Urethane Foam	MSA	Components may be promising, if formulation is modified for shorter setting time*
Urethane Foam (Stafoam)	Expanded Rubber and Plastic	Setting time of basic components much too long; very promising when modified for shorter setting time*
Urethane Foam (Autofroth)	Olin	Several formulations available; promising characteristics
Polyurethane Putty (Urabond)	Poly Resins	Sets up slowly on exposure to moisture or liquid water
Epoxy Putty (Polypoxy)	Pettit Paint	Setting time too long*
Epoxy Putty (Epoxylite 3351)	Epoxylite Corp.	Setting time too long*
Epoxy Putty (Sea Goin'-Poxy Putty)	Permalite Plastics	Promising (shorter setting time still needed)*
Steel-filled Epoxy Putty (Devcon SF)	Devcon Corp.	Sets up fairly rapidly to form high-strength solid
Lead-filled Epoxy Putty (Devcon L)	Devcon Corp.	Sets up fairly rapidly to form high-strength solid
Polysulfide Rubber Putty (EC612)	3M	Low strength requires backing for permanent seal
Butyl Rubber Sealer (EC1202-T)	3M	Too weak in tape form for permanent seal
Swelled Uncompounded Neoprene Rubber	Rocketdyne Preparation	High flexibility helps plug irregular holes but is extruded slowly by hydrostatic head
Rapid-curing Silicone Rubbers	Polysil	Several formulations tested; insufficient rigidity to seal large holes

*Setting times of less than about 10 seconds are desired

TABLE 2. HAZARDOUS CHEMICALS TESTED AND SMALL-SCALE SEALING TEST RESULTS

Hazard Ranking (Ref. 2)	Hazardous Material	Results of Sealing Tests		
		Stafoam Urethane Foam	Sea-Goin' Epoxy Putty	Other Sealants
1	Phenol	Sealed (A)[†*]	Failed (A)	Butyl Rubber-Sealed (A)
2	Methyl Alcohol	Sealed (A,W)	Sealed (A,W)	Epoxy Putty-Sealed (A) MSA Urethane-Sealed (A)
3,8, 14, 18	Insecticides, Rodenticides:			
	DDT 95% Solu./Water		Sealed (W)	
	Dieldrin	Sealed (A)	Sealed (A)	
4	Acrylonitrile	Failed (A)	Failed (A)	Polysulfide Rubber-Sealed (A)
5	Chlorosulfonic Acid		Failed (A)	
6	Benzene	Sealed (A,W)	Sealed (A,W)	MSA Urethane-Sealed (A,W)
9	Phosphorus Pentasulfide		Failed (A)	
10	Styrene	Sealed (A)	Sealed (A)	
11	Acetone Cyanohydrin		Sealed (A)	
13	Nonyl Phenol	Sealed (A,W)	Sealed (A,W)	
15	Isoprene	Sealed (A)	Sealed (A)	
16	Xylene		Sealed (A)	
17	Nitrophenol	Sealed (W)	Sealed (W)	

[†]Sealed leaks of aqueous solutions (50 to 90 percent) for 18 hours, then failed.

[*]"A" and "W" indicate tests performed in air and submerged in water, respectively.

was accomplished. Both chlorosulfonic acid and phosphorus pentasulfide could not be sealed. These chemicals probably require a very special sealant because they may be too reactive with water to permit practical sealing. Most of the other top 20 hazardous chemicals can probably be sealed with any sealant that is effective with either benzene or phenol. For example, sealants useful for benzene leaks would also likely be effective against the other hydrocarbons, styrene, isoprene, and xylenes. Sealants useful for phenol would probably also seal acrylonitrile and acetone cyanohydrin.

As indicated previously, some of the systems evaluated, both the expanding and nonexpanding types, react to yield crosslinked products. For the epoxies and urethanes, these crosslinking reactions are base catalyzed. Therefore, acid interferes with the reaction and attacks the crosslinked product. Thus, while these cured sealants may plug leaks of nonpolar chemicals, they are unsuitable with phenol or acrylonitrile. The failure to seal may be due either to the phenol, which is acidic and interferes with the cure, or the lack of resistance even of the cured sealants to these potent solvents. The temporary (18 hours) sealing of phenol by a urethane foam reported in Table 2 indicates that for this specific system, lack of resistance to the solvent is the mode of failure, rather than inadequate curing.

The four different types of rubber tested are inert to phenol and, therefore, could seal phenol leaks. However, they swell or dissolve in aromatic hydrocarbons. Uncompounded Neoprene W (Elastomer Chemicals, DuPont Corporation, Wilmington, Delaware) was allowed to swell in either carbon tetrachloride or benzene, forming a relatively soft, highly spongy mass before testing as a sealant. In this condition, it successfully sealed a 2-inch-diameter hole near the bottom of a 5-gallon drum full of water. However, the material still had a finite viscosity and so was slowly extruded through the hole; a permanent seal was required to prevent the leak from redeveloping.

One technique developed and tested to improve the ability of the nonexpanding materials to "bridge" a hole was to use a supporting or backing material. In its simplest form, this concept involved use of a "patch" in which the sealant was coated on the supporting fabric (e.g., nylon cloth) and the patch was then applied to the leak. Another 2-inch-diameter hole was permanently sealed by first applying a plug of the poly-sulfide rubber putty (3M Sealer EC-612, Minnesota Mining and Manufacturing, Minneapolis, Minnesota), followed by a patch of Sea Goin' Poxy Putty (Catalog Number 1324, Permalite Plastics, Costa Mesa, California) on a strip of nylon cloth that encircled the container. Several silicone rubber formulations were investigated using the nylon cloth technique. They had excellent chemical resistance, and it was possible to shorten the curing time to the order of 10 seconds; however, the mechanical properties (primarily rigidity and adherence) were not satisfactory for plugging leaks.

The "instant foams" consist of a polymer dissolved in a very low-boiling solvent and contained in pressurized cylinders. Upon opening a valve, a solid foam is formed very quickly. These foams were not promising for leak sealing, primarily for two reasons: the extremely fast solidification of the foam and the lack of any significant degree of adhesion to metal surfaces. Attempts to use these materials to seal leaks by forming mechanical plugs were not successful. While it is conceivable that other higher-boiling solvents could be used which would vaporize at a slower rate and thus delay setting of the foam, the current high cost of the foams and their limited availability led to the decision not to pursue this approach further.

A number of the potential sealants had some desirable characteristics, e.g., they either filled irregular holes, adhered well to metal, cured rapidly, or gave a strong cured product. However, for most of the solvents, at least one or more of these properties was seriously unsatisfactory. As a result of these tests, it was concluded that the urethane foams had the most potential for use in the larger-scale tests. This decision was based not only on the considerations enumerated above, but also on such factors as the ability to dispense large volumes of foam. This is of vital importance in large-scale tests.

SECTION IV

SCALEUP TESTS AND FEASIBILITY DEMONSTRATION

The primary purpose of this phase of the program was to evaluate the ability of a foamed system to plug leaks from larger holes and under conditions where the hydrostatic heads were greater than those encountered in the laboratory tests. Other factors that were examined included: barrier type (e.g., patch, outside plug, plug expanded outside and inside), thickness of barrier, speed of application, type of applicator, technique of application, and temporary support during the curing stage.

Much of the preparation of foams in this phase employed hand mixing in beakers. This technique was used to permit rapid evaluation and accurate control of composition of the foams in these tests. By weighing out the ingredients and then hand-mixing, the ratio of components could be carefully controlled with little effort. However, it was obvious that to employ this concept practically, a more flexible mixing/delivery system was required. Since no available mixing system was found that could perform the necessary functions, a system was designed and constructed (Fig. 1). It uses a 1/4-inch diameter in-line static mixer (Kenics Corporation, Danvers, Massachusetts) and can continuously supply a mixed, metered, two-component product over a range of small flowrates (up to about 1 lb/min). There are three chemical supply cylinders, fabricated of 2-inch-diameter, stainless-steel tubing approximately 12 inches long; two were used for the foam constituents and the third was used for a solvent with which the system could be flushed (methylene chloride was used as the solvent with urethane foams). An inert gas pressurization system was provided (nitrogen was used) to transfer chemicals from the supply cylinders. This device was used for tests with urethane foams, and could have been modified to permit its use with more viscous systems, such as the epoxy formulations. This mixing system was used only for a limited number of tests because it quickly became desirable and possible to progress to a much larger scale.

Early tests in this phase indicated that a key to successful plugging of large holes against appreciable hydrostatic heads is the expansion of the foam both inside and outside the hole to form a structural bridge. To achieve this, it is necessary to apply the foam at a point in its curing cycle where the foam is sufficiently mobile so that it can flow through the hole into the container and then expand to provide a bridge across the opening. However, during this stage, the foam must also have sufficient internal cohesion so that the chemical pouring from the container does not wash it away by mechanical action. It is desirable for the foam to be still capable of adhering to the container surface so that an intimate and strong bond can be achieved. These requirements led to the concept of either a special applicator design (large cross section, long residence time) or a two-stage application technique. In the latter concept, the foam is mixed externally and allowed to cure for a few seconds until it reaches the right stage of tackiness. It is then applied to a leak with some type of device that provides temporary support for an additional few seconds until sufficient rigidity has developed.

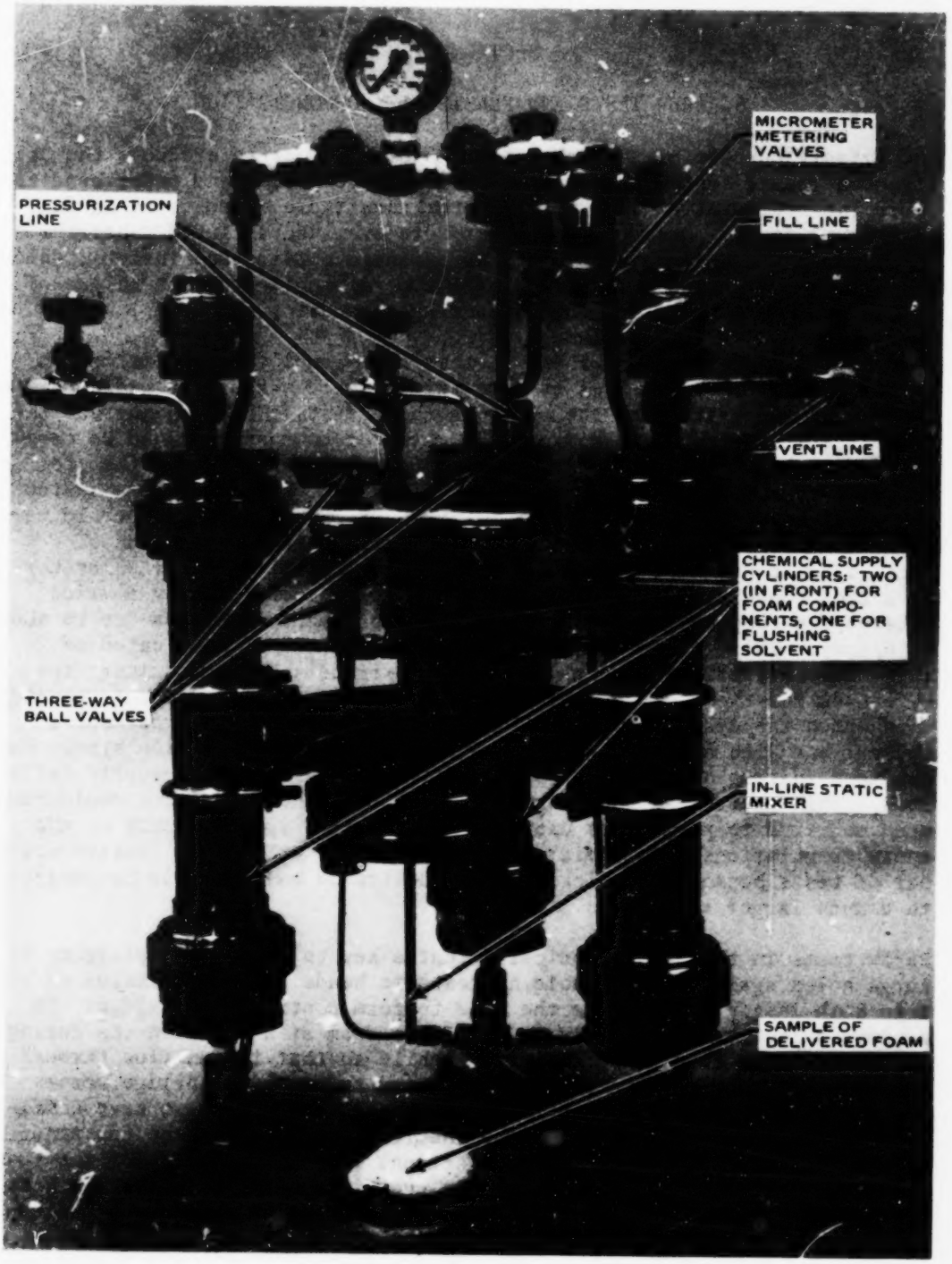
MICROMETER METERING VALVES
PRESSURIZATION LINE
FILL LINE
VENT LINE
CHEMICAL SUPPLY CYLINDERS: TWO (IN FRONT) FOR FOAM COMPONENTS, ONE FOR FLUSHING SOLVENT
THREE-WAY BALL VALVES
IN-LINE STATIC MIXER
SAMPLE OF DELIVERED FOAM

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Figure 1. Laboratory Mixing/Delivery System for Potential Sealants

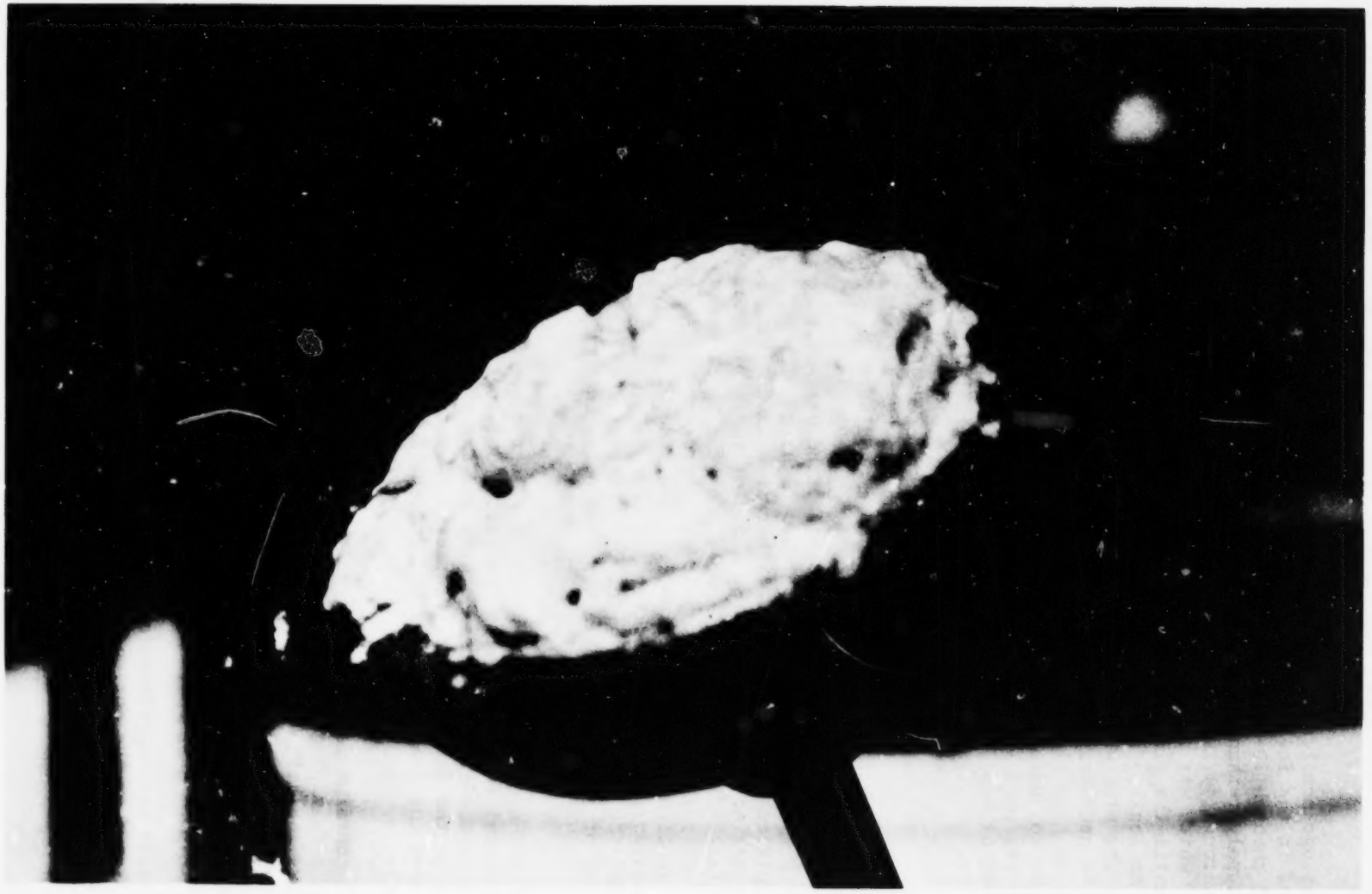
This two-stage application technique was tested in two simple forms (described in the following paragraphs), with considerable success. Figures 2 through 10 illustrate some of the large-scale tests that were made with polyurethane foams. The simplest of the two applicator forms (Fig. 2 through 4) involved the use of a large suction cup ("plumber's helper"), which was filled with foam that was allowed to set for a few seconds until the proper tackiness was reached. The cup was then placed against the leaking stream and some of the foam was forced through the hole with the plunger. The sides of the cup provided enough restraint so that the necessary compression of the foam cells could be achieved, resulting in expansion on the inside of the hole. It was not necessary for the cup to conform exactly to the surface of the container. This technique was used successfully to seal a 3-inch hole in a 55-gallon drum with 3 feet of head. It was also used successfully to seal 3-inch underwater leaks. Figure 2 shows a rubber plunger filled with foam prior to use. In Fig. 3, the plunger is being used to plug a 1-1/2-inch-diameter hole in a 55-gallon chemical drum. Two completed seals are seen in Fig. 4. In some cases, the rubber plunger cap adhered to the seal and was left in place but, in other cases, it could be removed after the foam set.

The second of the two applicator forms tested was a simple version of a piston in a cylinder, shown in Fig. 5. A charge of premixed but uncured foam was placed in the cylinder, either from hand mixing or from an in-line foam-mixing gun. Then the open end of the applicator was placed over the leak. Although Fig. 6 and 7 show the operator moving the applicator directly into the liquid jet, it is preferrable in some cases to move the applicator into position from the side of the jet. Then, with the applicator in place, the piston is moved to force the foam against and through the leak opening (Fig. 8). Figures 9 and 10 show the completed seal of this 3-inch-diameter leak using the Stafoam polyurethane foam.

Using the technique described above, a silent color motion picture (Ref. 3) showing several tests involving the sealing of leaks of benzene, methanol, and water from 55-gallon drums both in and out of water was prepared and submitted to the Environmental Protection Agency. This film graphically demonstrates the feasibility of the concept for plugging leaking chemical containers.

Figure 11 contains four frames from this motion picture, showing the formation of a foam plug in air, viewed from inside the container. The first frame shows the hole, looking from the inside of the container, with the liquid flowing outward. In the second and third frames, the foam plug and gas bubbles can be seen leaving the foam surface. In the fourth frame, the plug is completely formed. The plug formation was very rapid--approximately 1/2 second for the entire process.

To illustrate the ruggedness of a foam plug, Fig. 12 shows additional frames taken from the motion picture. After the outside portion of the plug is sawed off and removed, the remaining portion of the plug inside



5DZ11-1/28/72-S1E

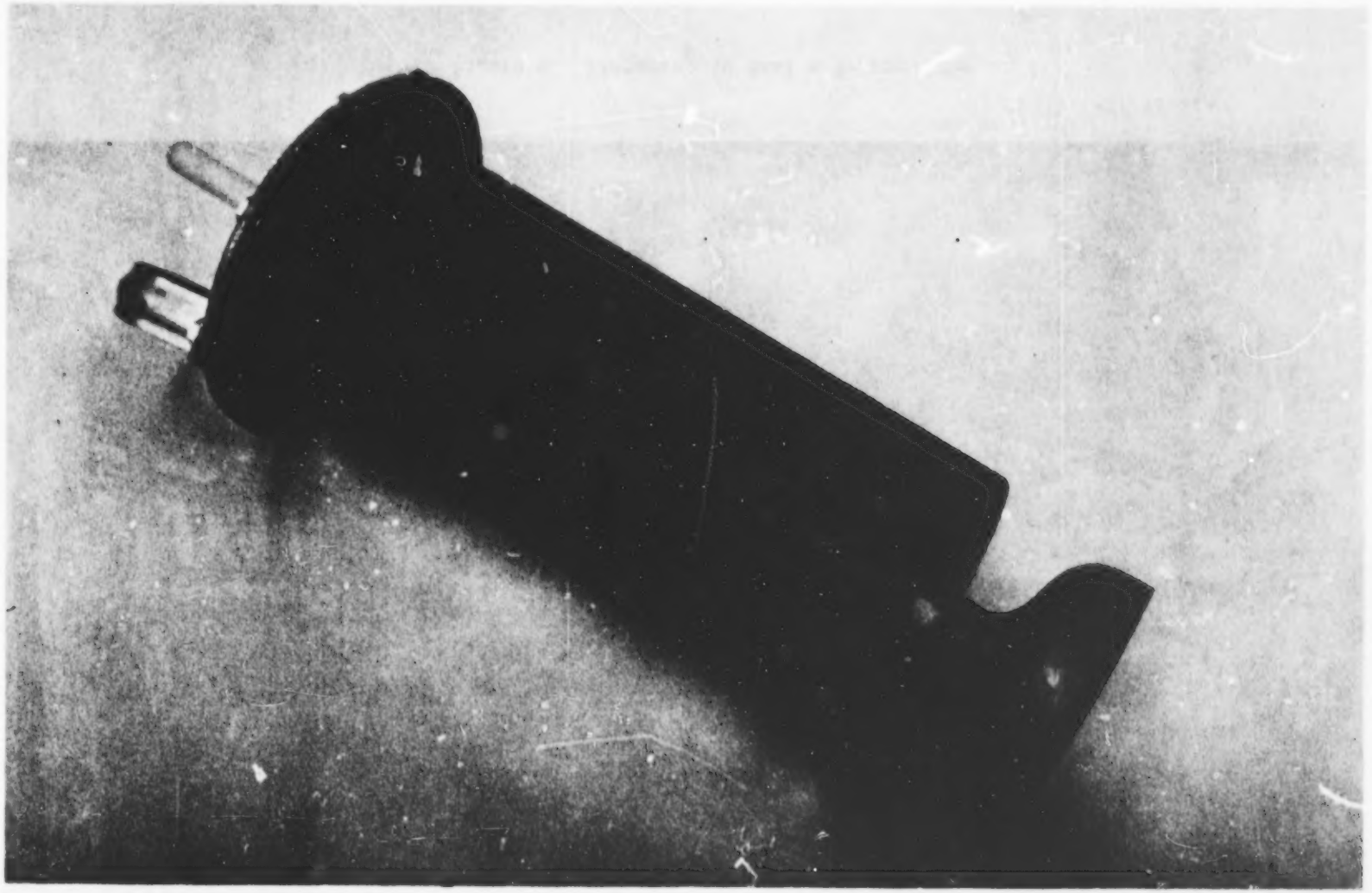
Figure 2. Simple Applicator With Foam

5DZ11-1/28/72-S1F

Figure 3. Sealing a 1-1/2-Inch Hole

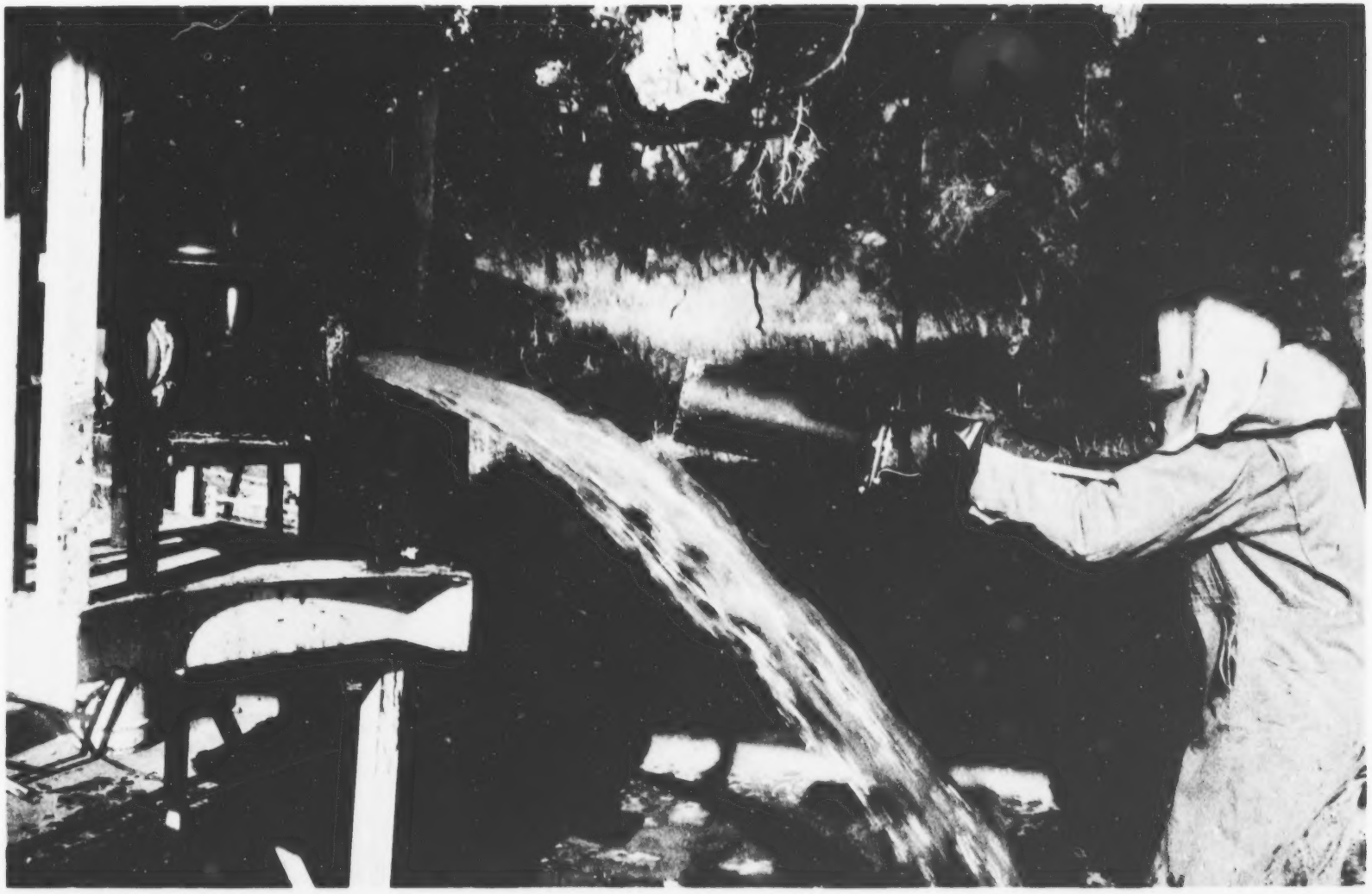
5DZ11-1/28/72-S1A

Figure 4. Completed Seals



5DZ11-1/28/72-S1D

Figure 5. Improved Applicator

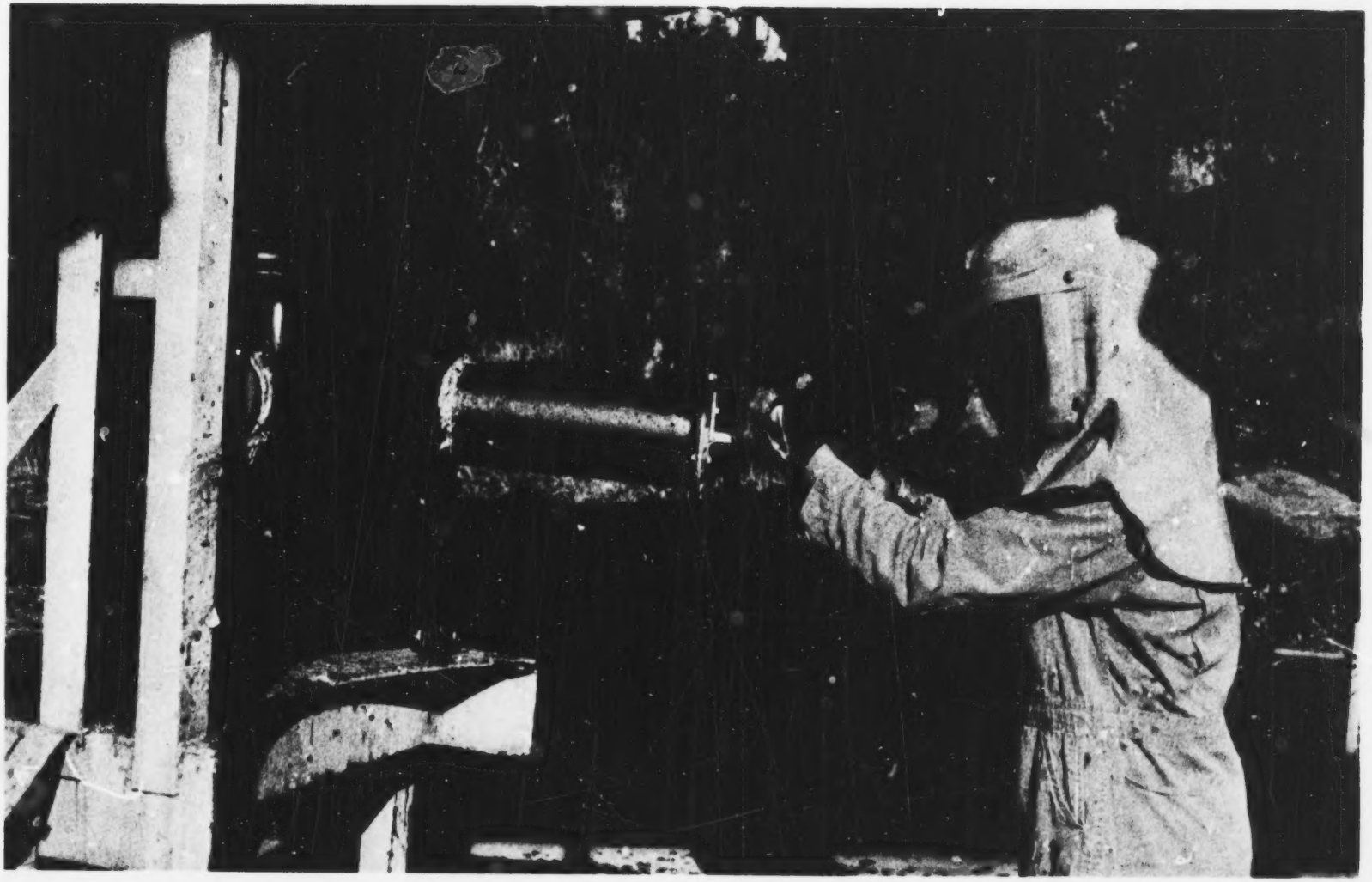


5DZ11-1/31/72-S1A

Figure 6. Preparing to Seal a 3-Inch Hole

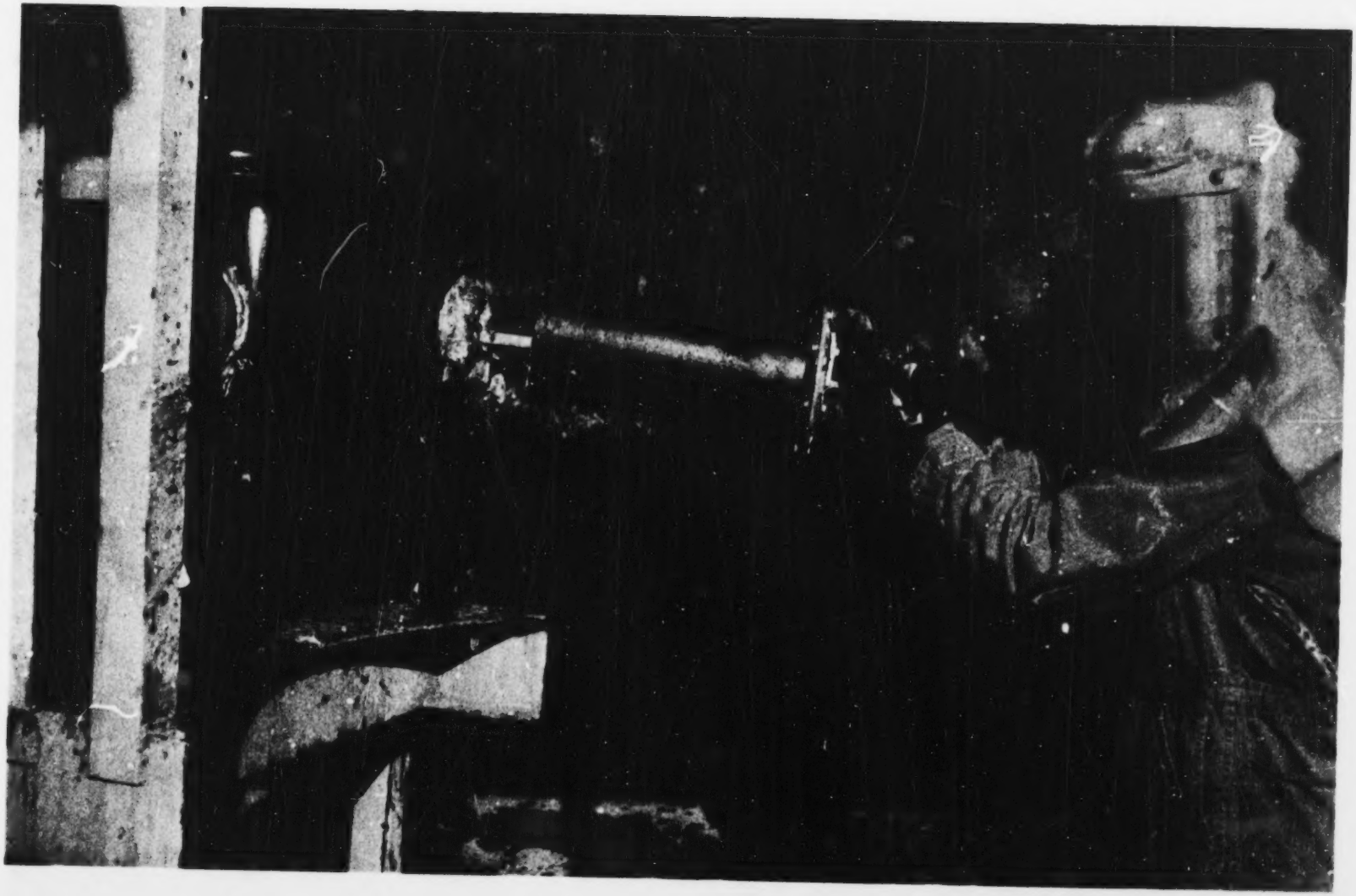
5DZ11-1/31/72-S1D

Figure 7. Moving the Applicator Into Position



5DZ11-1/31/72-S1C

Figure 8. With Plunger in Place, Foam is Extruded Into the 3-Inch Hole



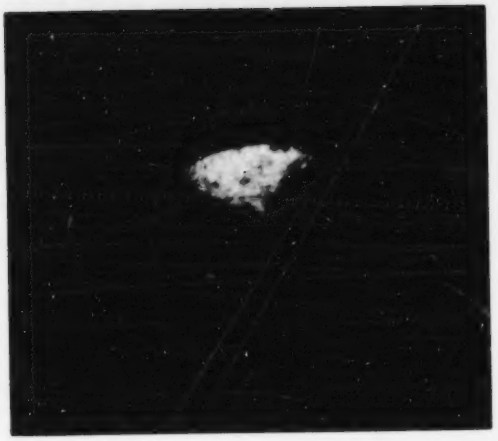
5DZ11-1/31/72-S1B

Figure 9. When Leak Has Been Stopped, Applicator is Retracted

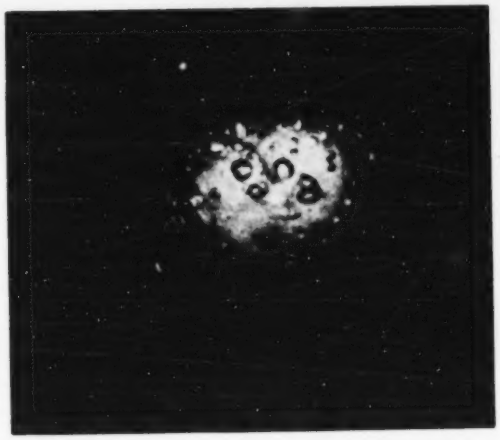
5DZ11-1/31/72-S1E

Figure 10. 3-Inch Hole Securely Sealed With Foam

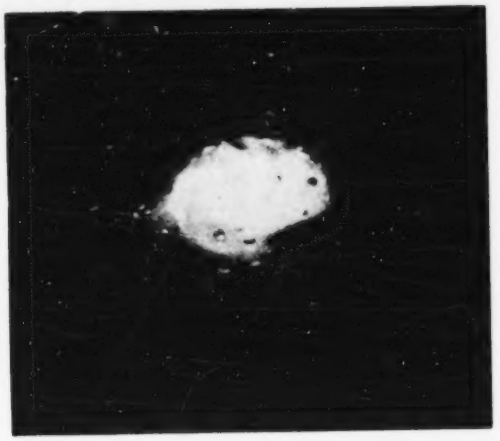
(a) Chemical is flowing outward through hole in container wall



(b) Foam is being applied from outside of container and starts to extrude through hole

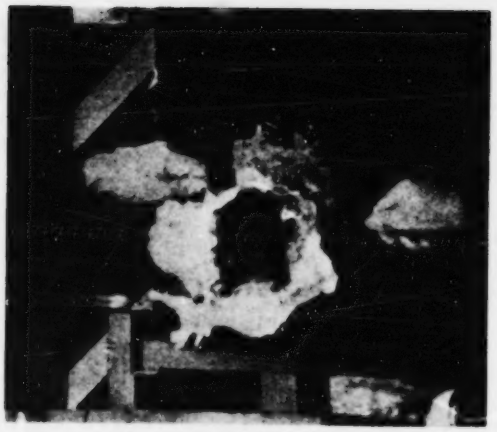


(c) Foam extrusion is completed; gas bubbles escape from curing foam



(d) Plugging is complete

Figure 11. Foam Plug Formation Viewed From Inside Chemical Container



(a) Completed foam plug is being sawed flush with drum outer surface

(b) Outer portion of foam plug is removed

(c) Remaining portion of plug inside container is sufficient to function as a seal

Figure 12. Ruggedness of Foam Plug

the container is sufficient to continue to function as a seal, as shown in the bottom frame in Fig. 12.

A benzene leak-sealing test in which the seal is applied underwater is shown in the sequence of photographs given in Fig. 13. The benzene can be seen gushing from the hole in the first frame. The application of urethane foam to seal the leak is shown in the second and third frames. The completed plug, lifted above the water surface, is shown in the fourth frame.

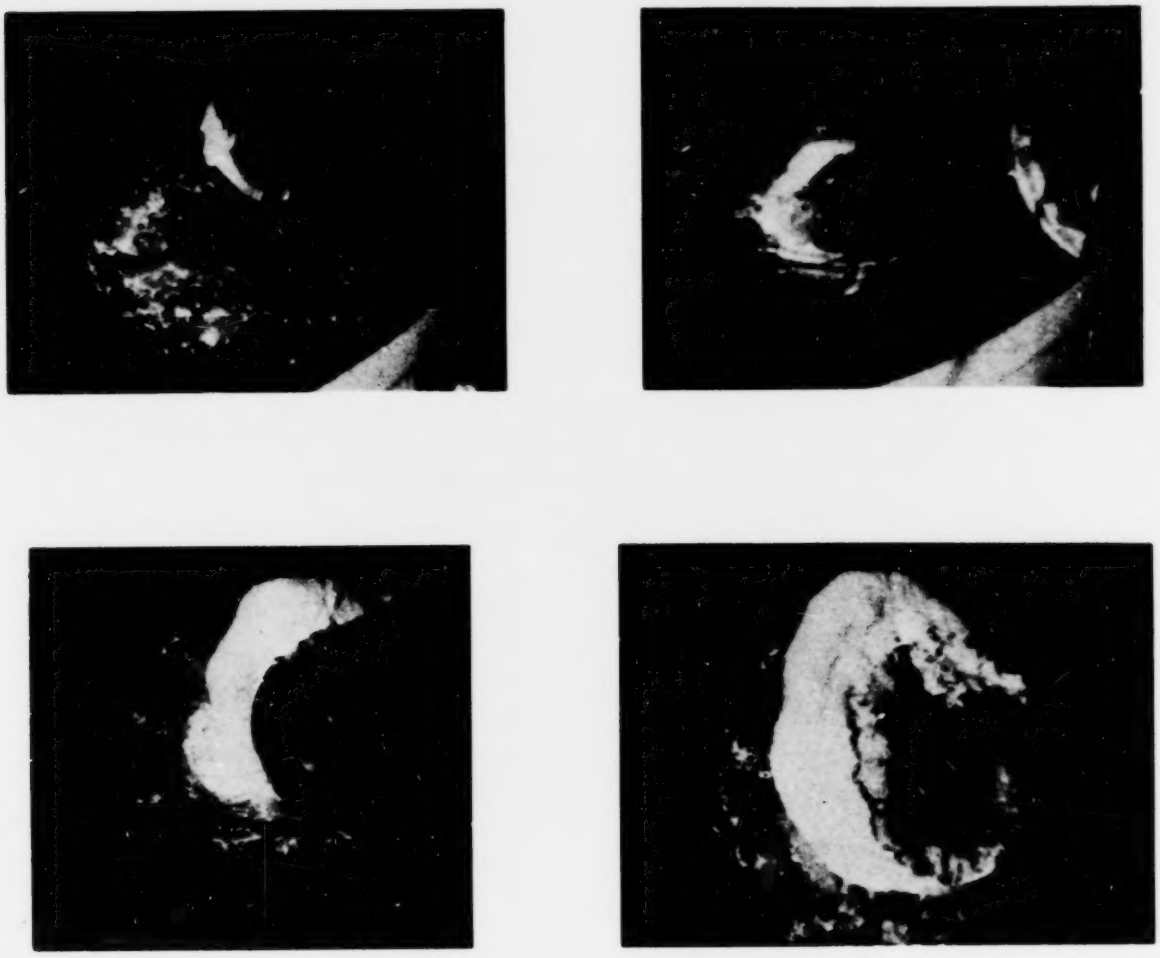


Figure 13. Benzene Leak Sealing Under Water

SECTION V

PRELIMINARY DESIGN AND DEVELOPMENT

Based upon the successful demonstration of the feasibility of the concept, preliminary investigative work was started toward eventual development of a system for operational use. This work is summarized in the following subsections, describing: the results of a study to assess the range of applicability of this type of leak-sealing system, a continual survey of available foam application hardware, preliminary development tests that were made, predictions of the hazardous chemicals which can be sealed, and some preliminary design concepts that were generated.

ENVELOPE OF PRACTICAL APPLICATIONS

A question of considerable importance is: What types of hazardous spills can be effectively treated by use of the sealing techniques being developed? A preliminary study was made to define an envelope of applicability in terms of characteristic parameters of a leaking container (size of hole, size of container, and liquid head in the container) within which this type of technique should be considered.

It is obvious that a very large hole in a small container will result in a complete loss of the contents before corrective action can be taken. Therefore, there is an upper limit on hole size (as a function of container size, liquid head, and response time) which it is practical to consider. Efflux times can be calculated for any given container geometry and orientation, hole size and location, and type of liquid. An analysis was made, using the following assumptions and definitions:

1. Leak sizes may be specified by a single characteristic diameter, D.
2. Containers have a cross-sectional area that does not vary with liquid height and is specified by a characteristic diameter, D_c.
3. Leaks occur at the bottom of the vessel.
4. The effective container height, H, divided by the characteristic diameter is a known value, e (generally less than the actual container height divided by the actual diameter).

The time required for the liquid level in the container to drop to some fraction (f) of H is (the derivation is given in the Appendix):

$$T = 8.21 \left[1 - (f)^{1/2}\right] \frac{V^{5/6}}{CD^2 e^{1/3}} \qquad (1)$$

where T is time in seconds, V is the initial container volume in gallons, C is the discharge coefficient of the hole, and D is given in inches.

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Using values of C = 0.61, T = 120 seconds, and f = 0.70 (i.e., losing 30 percent of the contents in 2 minutes), the resulting relationship between the leak size and the size of a container is:

$$D = \frac{0.135\ V^{5/12}}{e^{1/6}} \qquad (2)$$

The results are plotted as curves A1 (for e = 1.5) and A2 (for e = 0.5) in Fig. 14.

Another boundary condition can be derived by considering the limits of human strength. It is assumed that the leak-sealing technique to be developed must be suitable for application by one man. Any of the systems envisioned at present would require that essentially all of the flow be stopped at once. This means that the operator must be able at least to exert a force sufficient to hold a plug in place against the hydraulic pressure of the leak for a few seconds. Alternatively, the force required to overcome the momentum of a liquid stream could be as much as 20 percent greater (see the Appendix for details); however, this can probably be reduced substantially by design of an applicator to deflect at least part of the momentum of the fluid stream. Consequently, the limiting constraint, based on human strength, was taken as the force required to withstand the static pressure of the leak. The maximum usable force which can be exerted in a horizontal direction by one man (F) is estimated to be 50 lbf. Using the same assumptions as before, a relationship can be derived (see the Appendix) for the maximum hole size that can be plugged in tanks of various sizes. For V in cu ft, D in feet, F in lbf, and the fluid density, ρ, in lb/cu ft, the relationship is:

$$VD^6 = \frac{16\ F^3}{\pi^2\ e^2 \left(\rho\ \frac{g}{gc}\right)^3} \qquad (3)$$

This equation (with ρ = 62.4 lb/cu ft and F = 50 lbf) is plotted as curves B1 (for e = 1.5) and B2 (for e = 0.5) in Fig. 14.

The area to the left of both curves A1 and B1 (for e = 1.5) or A2 and B2 (for e = 0.5) is then the applicable area for development of leak-sealing techniques. It should be noted that the assumptions used are "worst case" (e.g., the hole was assumed to be at the bottom of the container, whereas it actually could be anywhere). Also, a circular hole was assumed, providing the greatest distance to be bridged by the sealant for a given leak size. The total region for practical applications of this concept is much broader than the limiting boundaries shown in Fig. 14.

The final consideration is to assess the capabilities of the actual leak-plugging techniques which will be developed (i.e., the maximum hole size/hydraulic head combinations that can actually be handled by the developed technique). It already appears promising, from the work of this project, that the method can be developed to the point of sealing leaks in most or all of the applicable region to the left of curves A and B in Fig. 14.

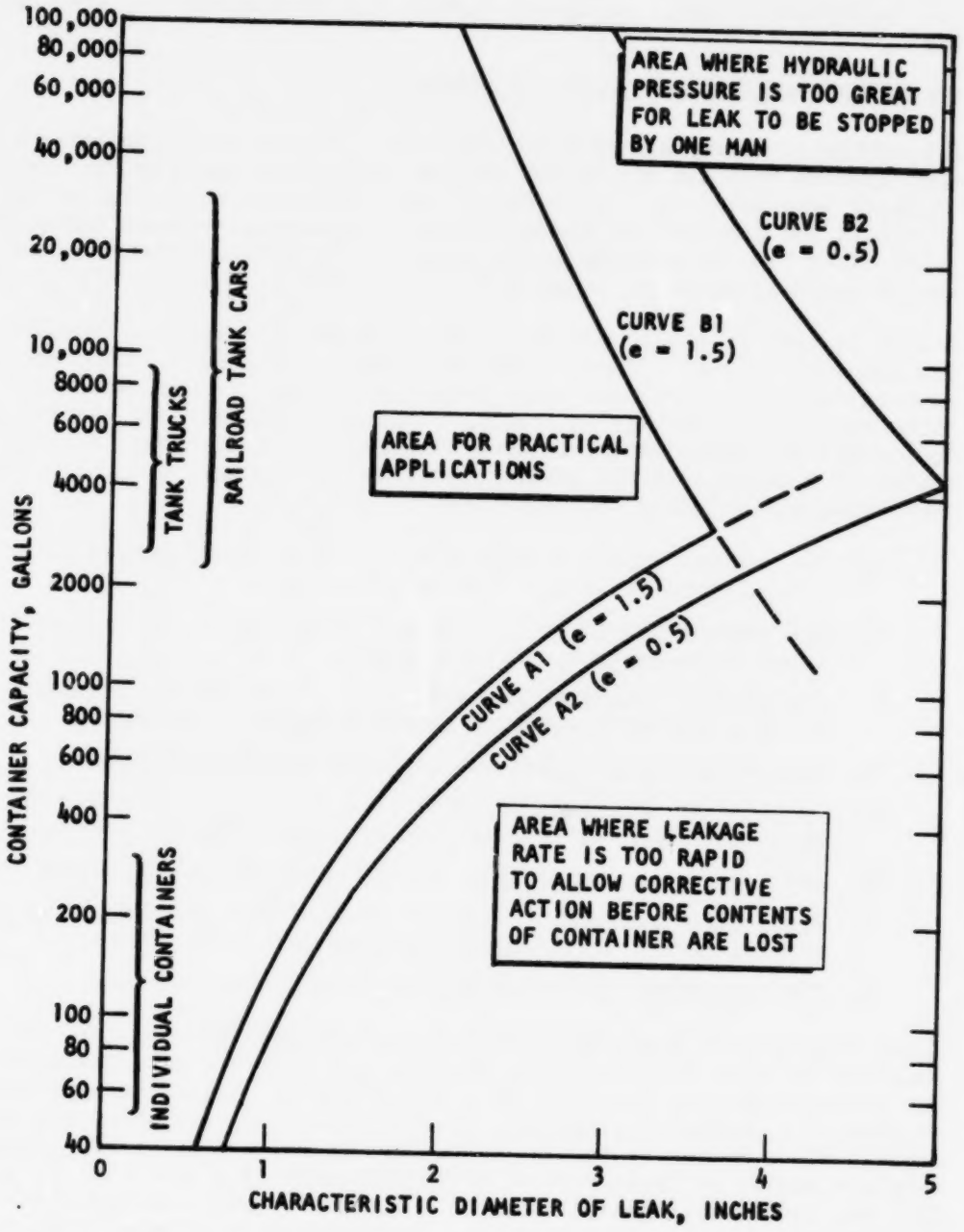

Figure 14. Envelope of Practical Applications for Sealing Leaks in Nonsubmerged Containers

The study outlined in this section indicates that the region of practical applicability is broad enough and the potential capability of the leak-sealing system is great enough to justify its development for operational use.

SURVEY OF AVAILABLE APPLICATION HARDWARE

A preliminary survey was made to investigate commercially available hardware systems that can mix and/or deliver foams, nonfoamed polymer systems, caulking materials, etc. This survey was limited in scope, but should be continued and expanded in connection with any subsequent development project. This type of information is important to make maximum effective use of existing hardware in any development work:

A wide variety of mixers and delivery equipment is commercially available for handling polymer systems of diverse types. In general, this equipment is designed to be used under rather different circumstances than those encountered in sealing leaking containers of hazardous materials. To prevent hazardous materials from contaminating a waterway, the application of a sealant to the leaking container should meet a number of requirements, including the following:

1. The sealant should be sufficiently flexible to conform to irregular holes in the leaking container.
2. The sealant should be (or become) sufficiently rigid to withstand appreciably hydrostatic heads.
3. The sealant should be chemically inert both to the hazardous material and with water to permit underwater sealing.
4. The sealant should have satisfactory temperature limits.
5. Application should be possible to a variety of container surface geometries and coatings (including dirty container walls).
6. Application should be made shortly after discovery of the leak.
7. Application should be performed without the operator exposing himself unduly to the hazardous material or its fumes.
8. The applicator should be self-contained and portable.

These requirements might be fulfilled with a number of sealants. The requirements that the sealant be flexible yet have a high yield stress can probably best be satisfied by a two-component sealant such as urethane systems. The unreacted components have a fairly low viscosity, but react rapidly after mixing to form high-modulus crosslinked polymers. Rapid, complete mixing of these systems after discovery of a leak will be essential for successful application. In the normal commercial applications of polymers, usually not for sealing leaks, emphasis is more often placed on long pot life (of the order of hours) so that the polymer can be mixed in larger batches and applied with ample time before it sets up. In

sealing leaking containers of hazardous materials, on the other hand, primary emphasis must be on plugging the leak rapidly to prevent pollution of the waterway. Both the choice of sealant system and application hardware must fulfill different functions than in usual commercial polymer applications. To provide background relative to the kinds of hardware development necessary for prototype design, some typical commercial polymer application equipment is described below.

One of the most directly applicable lines of mixers and delivery equipment that have been identified is supplied by Semco, a division of Products Research & Chemical Corporation (Glendale, California). Their equipment line includes air-powered and mechanical caulking and sealant guns that use disposable sealant cartridges containing from 2-1/2 to 12 ounces of material. These guns are portable, especially when the air-powered ones are driven with a self-contained portable cylinder of gas, which is also marketed by Semco. Another of their important services consists of prepackaging custom-designed two- and three-part sealants in disposable cartridges that fit their guns. The various components are mixed in the cartridge, just before application, using equipment also supplied by Semco (but which requires an electrical power source). The applicators are all simple nozzles; however, openings are available covering a range of sizes and shapes from a 27-gage needle to one with a rectangular opening 1-3/4-inch wide.

Equipment similar in function and size range to that supplied by Semco is also marketed by Pyles Industries (Wixom, Michigan). Another line of urethane foam delivery equipment is available from the Olin Corporation Plastics Division (Brookpark, Ohio). These have many desirable features. This kind of delivery hardware sold by Semco, Pyles, and Olin more nearly approximates the needs for sealing leaks in containers of hazardous chemicals than any other equipment about which information has been obtained; however, their characteristics are not unique.

Much other equipment is available for mixing and applying various cross-linking polymer systems such as epoxies and polyurethanes. Most of this hardware is apparently designed for much larger-scale delivery than is desirable or necessary for the one-shot production of a seal for a leaking container. For example, Glas-Craft of California supplies a "portable spray-up system" for the application of glass-reinforced polyester resin at the rate of 20 lb/min of laminate. This apparatus is hardly "portable"; the shipping weight is approximately 400 pounds. A somewhat smaller gel-coat system marketed by the same supplier is also mounted on a cart, and both systems are electrically driven. Similar comments about portability and electrical power requirements can be made about equipment supplied by the Sealzit Division of Flintkote Company (Riverside, California), Gusmer Corporation (Hoboken, New Jersey), and Hardman Incorporated (Belleville, New Jersey). Other companies contacted whose equipment was unsuitable for sealing leaking containers rapidly included Hunt Process Company (Santa Fe Springs, California), Grover Pump Company (Montebello, California), and Zepco Manufacturing Company (Burbank, California).

Although the Semco, Pyles, and Olin equipment are perhaps the best of these investigated (i.e., the most directly applicable to plugging leaking chemical containers) and include equipment with many useful features, none of them satisfy all of the requirements needed for the applications that are the subject of this program. The most serious deficiency is that only simple nozzles are available for use as the applicator. This type of nozzle is perfectly satisfactory for the intended purposes of the equipment, but is completely unsuitable for use in plugging difficult leaks of hazardous chemicals. A second deficiency (in the case of multicomponent sealants) is that the available mixing arrangements are neither portable or self-contained (electric power is necessary to drive a mixing motor). A third deficiency, for adaptation to plugging leaks, is that the available systems all have a very short distance between the control point for sealant flow (typically a trigger arrangement) and the delivery point. The operator of the sealant applicator would, therefore, necessarily be too close to the leaking hazardous material. Greater separation would be necessary for safety.

The conclusion that suitable equipment for the present application is not "off the shelf" w further confirmed by a number of individuals thoroughly familiar w.. the industry, including personnel at Hardman Incorporated, Permalite Plastics (Costa Mesa, California), and NASA-Ames.

None of the hardware systems thus investigated is completely suitable for the requirements of plugging leaks of hazardous chemicals. However, some of the components and features will be useful in subsequent development work, and should be utilized wherever this is practicable.

PRELIMINARY DEVELOPMENT TESTS

During the scaleup tests, the large suction cup (plumber's helper) was used as a foam applicator with considerable success in sealing a 3-inch hole in a 55-gallon drum with 3 feet of head. The basic plumber's helper technique was then improved and the plunger-in cylinder technique was developed. In this improved technique (which was shown in Fig. 5 through 10 and in the movie film), a length of Teflon pipe was used as a cylinder. The portion of the cylinder above the plunger was filled with foam, the open end of the cylinder was placed over the leak and the plunger was used to force foam against and through the hole in the leaking container. This application technique, even in its simplest form, was quite successful in eliminating some of the previous problems associated with deflection of the applicator and foam.

Not all tests were successful with the plunger-in cylinder technique. Experience gained during the testing identified several problems associated with the technique of application, one of which was control of the pressure exerted during application. The appearance of that portion of the foam extruded through the hole in some unsuccessful leak sealing tests showed that the seal was broken by forcing more foam through the hole after the foam had set up. No consistent relationship could be observed

between the force exerted on the applicator plunger and the appearance of the foam after the test, since most of the force was consumed in overcoming internal friction in the applicator. Although the applicator barrel was made of Teflon, adhesion of foam to the inside surface produced enough friction to make it impossible to empty the applicator after a certain degree of cure had been reached. This problem was eliminated by a modification of the application technique in which the applicator barrel was lined with a thin, disposable polyethylene bag. The foam was placed into the bag, and the plunger then forced the foam out of the bag with only negligible friction between the polyethylene and Teflon surfaces. Using the modified technique, it was possible to exert a uniformly reproducible pressure on the foam at the hole. An additional advantage achieved by this change in applicator design was that the rubber base of a plunger was no longer in contact with the foam and therefore was not bonded to it. The plunger then served as a piston to eject the foam from the applicator, and the plunger cound be removed entirely after application of the foam to the leak.

The need for controlling and adjusting the foam composition to obtain better seals with a specific chemical was demonstrated in many of the scaleup and preliminary development tests in which the Stafoam polyurethane system was used. This foam system consists of: (1) a hydroxyl-containing polymer ("polyol"), (2) an isocyanate (toluene diisocyanate) or a mixture of toluene diisocyanate and other polyisocyanates, and (3) a low-boiling fluorocarbon. In addition, an amine (e.g., triethylamine) is dissolved in the polyol and serves as a catalyst for the crosslinking reaction between the polyol and the isocyanate component.

Structurally, the polyol is an aliphatic polyester with hydroxyl end groups and, therefore, is susceptible to solution by polar chemicals (e.g., methanol). By contrast, the isocyanate is aromatic in nature and more likely to be dissolved by benzene, toluene, or xylene. If a successful seal is to be made against a specific chemical, such factors must be taken into account.

The Stafoam components as provided by the supplier are recommended for use at 85:100 isocyanate to polyol weight ratio. At this level, the seals obtained against benzene leaks were fairly good. However, superior seals were produced when the isocyanate component ratio was increased to 95:100. This may seem somewhat surprising in that, with the aromatic nature and the increased content of the isocyanate component, this composition should be more susceptible to attack by benzene. However, this is more than compensated for by the larger degree of crosslinking obtained at the high isocyanate level. With this formulation, even better seals could be obtained by speeding up the crosslinking reaction by adding 4 milliliters of triethylene to 195 milliliters of the combination. This is advantageous in that the action of benzene on the composition is only that of a solvent for the isocyanate component. By speeding up the crosslinking reaction, the time available for the benzene to dissolve unreacted isocyanate is markedly reduced. This results in a better foam.

The sealing of a methanol leak is complicated by its chemical reactivity with the isocyanate. To compensate for this, additional isocyanate was added to bring the isocyanate:polyol ratio to 100:100. This provides another advantage in that the increased quantity of isocyanate reduces the solubility of the polyol in methanol. However, for successful sealing of methanol leaks, it was found necessary to speed up the curing reaction substantially. Thus, 7 to 8 milliliters of triethylamine were added to every 200 milliliters of the foam combination.

Seals of the modified Stafoam combination held up in benzene for well over 24 hours with no evidence of deterioration. The modification developed for methanol exhibited signs of attack by methanol after 8 to 12 hours of exposure. Small-scale seals with the hazardous chemicals tested were generally intact after at least several days.

To progress to the next steps in developing practical leak-sealing systems, it was necessary to obtain the foam components in pressurizable containers. The polyurethane foam system that was used in most of the scaleup tests was the Stafoam product of Expanded Rubber and Plastics Company (ERP). This was the most suitable urethane of the foam systems that had been screened. However, the components were available only in bulk; therefore, it had been necessary to mix the components by hand in an open container. Attempts were made to obtain these components in pressurizable cylinders; however, this was not possible within the time requirements of the program. After examination of the alternatives, it was decided to obtain a froth polyurethane foam system (Autofroth I) from Olin which was very similar to the improved foam which was recommended by ERP.

With the components in pressurizable cylinders and with the use of a mixing gun, it was possible to supply the foam directly into the leak-seal applicator previously used. It was found that the foam properties and leak-sealing performance of a given system were much better when used in this mode than when mixed by hand. Figures 15 through 17 show urethane components in pressurizable cylinders and a mixing gun built by Rocketdyne. This gun was a working tool (not a development item) and continued to evolve during its use, as described in the following three paragraphs. The sequence in Fig. 17 illustrates the initial increase in foam volume as it begins to cure.

A series of tests was made using Olin urethane systems and the Rocketdyne mixing gun. In the first few tests, it was obvious that poor mixing of the polyol and isocyanate was obtained. An increase in cylinder pressure (to increase the velocity of the impinging streams) plus a change in the size of the gun's "mixing element" did not noticeably improve the results. In addition, partial plugging of the mixer element was occurring. Several tests were conducted and one successful sealing test was made on a 2-inch-diameter hole in a 5-gallon can filled with water. This was followed by a number of unsuccessful attempts at sealing benzene. The first Olin foam formulation tested (designated C-2) has a relatively long cure time

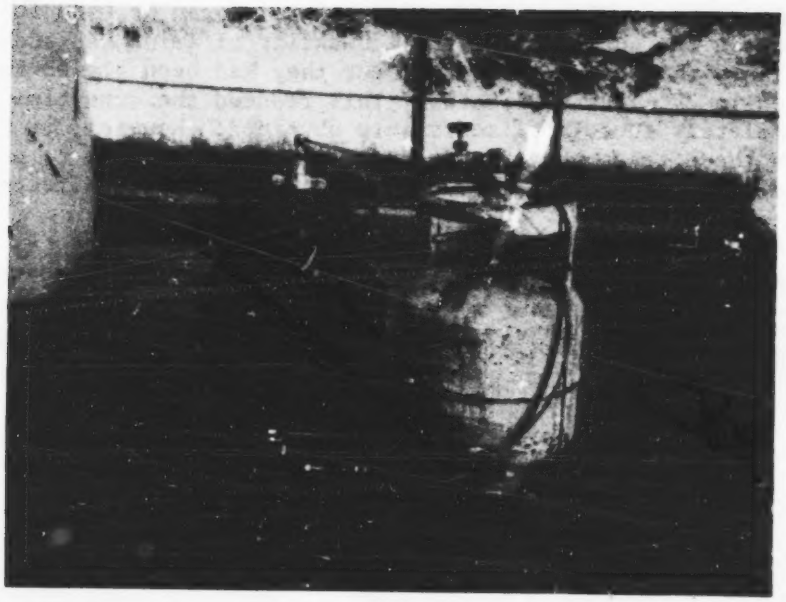

Figure 15. Pressurizable Foam Cylinders With Rocketdyne Mixing Gun

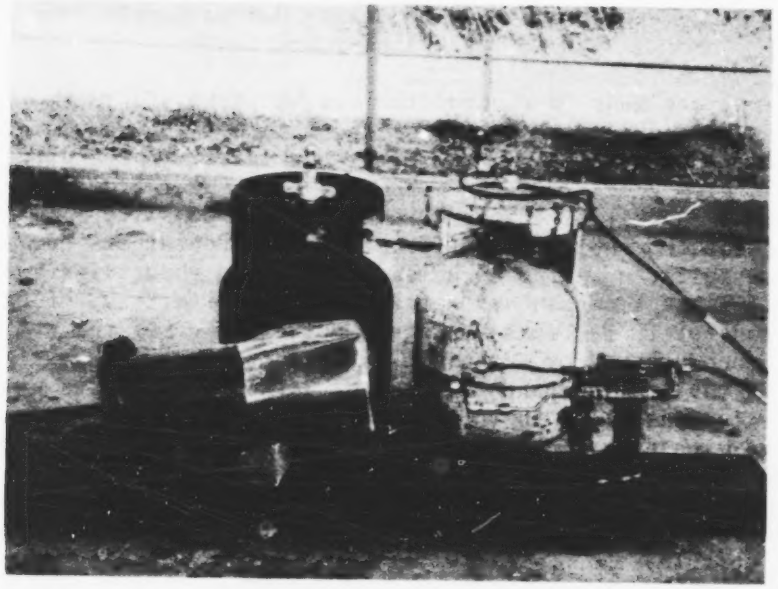

Figure 16. Pressurizable Foam Cylinders, Mixing Gun, and Polyethylene-Lined Plunger-In-Cylinder Applicator

(on the order of 20 to 30 seconds) before it can be used for sealing. To shorten the cure time, a small quantity of amine was added and hand mixed into the foam components after they had been placed into the plunger-in-cylinder applicator. This reduced the cure time, but still no completely successful seals were obtained. However, it became apparent in these tests that the weight ratio of isocyanate to polyol (which should be nominally 1:1) was high and thus adversely affected the properties of the foam.

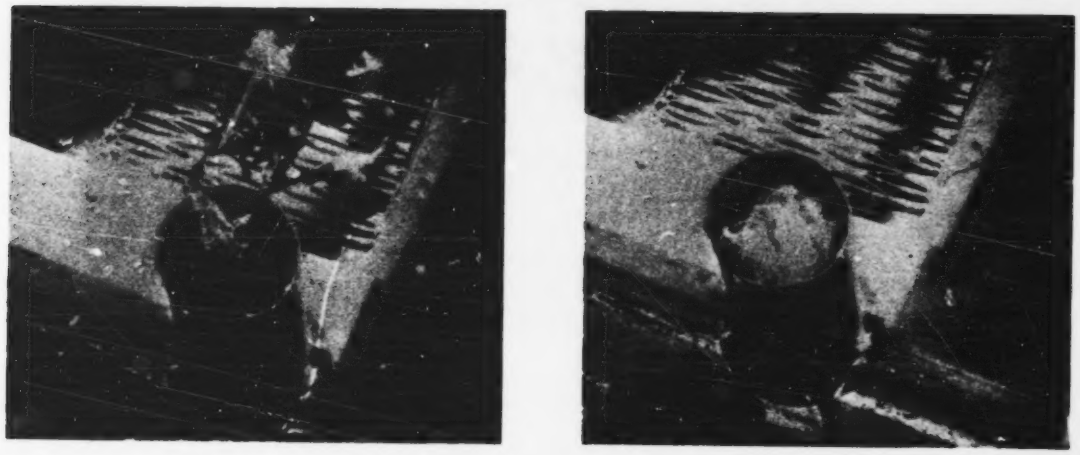

Figure 17. Use of Mixing Gun to Supply Foam to Cylinder Applicator

An attempt was made to control the weight ratio of the two foam components (isocyanate and polyol) by installing a throttling valve between the isocyanate cylinder valve and the mixer gun valve. Short-duration (2 to 3 seconds) flow checks were made to determine the ratio of the two foam components. The flow checks were simple and consisted of simultaneously flowing the two individual streams into two containers and weighing the material collected. The technique of using a throttling valve to control the isocyanate flowrate was not entirely satisfactory. Flow checks had to be made every few runs and, in a number of cases, the ratio had changed. A new procedure and/or technique must be developed to maintain the desired ratio of the foam components. In the leak-sealing tests with the throttling valve installed in the isocyanate line, two successful seals were obtained with each of the two test fluids (water and benzene). Seals were made on a 2-inch-diameter hole in a 5-gallon container. In these tests, no mixing element was used on the mixing gun. The foam components were introduced directly into the plunger-in-cylinder applicator and mixed with a spatula.

Tests were next made using a Kenics static mixer in the gun. This component basically consists of a straight section of tubing containing a series of metal ribbons, twisted about an axis coincident with the tube centerline, and designed to repetitively subdivide and comingle segments

of the flow, thereby causing mixing as the fluids flow through the tube. Also, a large in-line mixer (similar to the Kenics static mixer) was constructed, incorporated into the mixing gun, and used in two benzene sealing tests. These tests were successful with respect to achieving adequate mixing; however, additional work will be necessary to improve the control of component mixture ratio.

The preliminary development test efforts just described comprised initial steps in the development of an operational system. This work can provide a foundation for a subsequent development program. The goal of a development effort should be to produce a system that operates satisfactorily anywhere within the envelope of practical application discussed earlier, and embodies the following characteristics:

1. Ability to completely plug leaks
2. Permanent or long-term plugging
3. Rapid response
4. Moderate weight and portability (use by one man)
5. Safe and easy to use by untrained personnel
6. Reasonable cost
7. Usable with liquid heads as high as those encountered in tank cars
8. Flexibility in hole size, shape, location, etc.
9. Usable with dry, dirty, and wet surfaces
10. Compatible with wide range of hazardous chemicals
11. Long shelf life
12. Wide temperature tolerance (both in storage and application)
13. No external power requirements (except possible use of compressed gas)
14. No secondary pollution problems
15. Allows salvage of hazardous chemical remaining in tank

CHEMICALS WHICH CAN BE SEALED

Many of the other high-hazard chemicals are chemically similar to those that were used in leak-sealing tests during this program. Tentative predictions were made of the expected behavior of the 100 most hazardous soluble chemicals (Ref. 1 and 2) toward polymeric sealants (particularly urethane foams). These predictions are summarized in Table 3. Where it is indicated that successful sealing is not probable, the decision was based on one or more of the following:

1. The compounds have excessively high vapor pressures at ambient temperature.

TABLE 3. PROBABLE LEAK SEALING SUCCESS WITH 100 HAZARDOUS CHEMICALS

Hazard Ranking, Ref. 2 (1 is most hazardous)	Hazardous Chemical	Can Probably be Sealed	Can Probably Not be Sealed	Prediction Not Yet Possible
1	Phenol	X		
2	Methyl Alcohol	X		
3	Insectides and Rodenticides, Cyclic	X		
4	Acrylonitrile	X		
5	Chlorosulfonic Acid		X	
6	Benzene	X		
7	Ammonia		X	
8	Misc. Cyclic Insecticides	X		
9	Phosphorus Pentasulfide		X	
10	Styrene	X		
11	Acetone Cyanohydrin	X		
12	Chlorine		X	
13	Nonyl Phenol	X		
14	DDT	X		
15	Isoprene	X		
16	Xylenes	X		
17	Nitrophenol	X		
18	Aldrin-Toxaphene Group	X		
19	Ammonium Nitrate	X		
20	Aluminum Sulfate	X		
21	Nitric Acid		X	
22	Herbicides and Plant Hormones, Cyclic	X		
23	Dyes, Total	X		
24	Tetraethyl Lead	X		
25	Ammonia Sulfate	X		
26	Fungicides, Total, Cyclic	X		
27	Sulfuric Acid		X	
28	Halogenated Hydrocarbons	X		
29	Phosphorus, Red	X		
29	Phosphorus, White		X	
30	2, 4-D Acid Esters and Salts	X		
31	Benzoic Acid	X		
32	Formaldehyde	X	X	(See text)
33	2, 4-D Acid	X		
34	Sodium Dichromate and Chromate	X		
35	Pesticides and Insecticides, Acyclic	X		
36	Tetramethyl Lead	X		
37	Ethers, Total	X		
38	Ferrous Sulfate	X		
39	Sodium Sulfide			X
40	Hydrochloric Acid		X	
41	Nickel Compounds	X		
42	Benzaldehyde	X		
43	Hydrogen Cyanide		X	
44	Butyl Alcohol, N- and Iso-	X		
45	Chlorinated Isocyanurates			X
46	Calcium Fluoride	X		
47	Hexamethylenediamine	X		
48	Fatty Acids	X		
49	Pyridine	X		
50	Lead Compounds	X		
51	Naphthalene	X		
52	Carbon Disulfide	X		
53	Hypochlorites			X
54	Calcium Hypochlorite			X
55	Copper Sulfate	X		
56	Sodium Hydroxide			X
57	Acids, Acylhalides and Anhydrides			X
58	Dodecyl Mercaptan	X		
59	Phosphoric Acid			X
60	Nitrobenzene	X		

TABLE 3. (Concluded)

Hazard Ranking, Ref. 2 (1 is most hazardous)	Hazardous Chemical	Can Probably be Sealed	Can Probably Not be Sealed	Prediction Not Yet Possible
61	Methyl Parathion	X		
62	Alcohols, Monohydric, Unsubstituted	X		
63	Chromic Acid			X
64	Aldehydes and Ketones	X		
65	Misc. Cyclic Herbicides	X		
66	Fluorine Hydrofluoric Acid		X	
67	Misc. Acyclic Insecticides	X		
68	Potassium Iodide	X		
69	Sodium Carbonate			X
70	Amines, Total		X	
71	Aniline	X		
72	Aluminum Fluoride	X		
73	Ammonia Compounds	X		
74	Carbon Tetrachloride	X		
75	Furfural	X		
76	Lindane	X		
77	Sulfur Dioxide		X	
78	Ammonium Perchlorate			X
79	Mercury Compounds	X		
80	Acetonitrile	X		
81	Toluene	X		
82	Trimethylamine		X	
83	Mercury Fungicide	X		
84	Lead Arsenate	X		
85	Ethyl Benzene	X		
86	Perchloric Acid			*
87	Methylamines		X	
88	Pentachlorophenol	X		
89	Sodium Hydrosulfite			X
90	Acetaldehyde	X		
91	Ammonium Chloride	X		
92	Ethylenediamine			X
93	Acetic Acid			X
94	Calcium Carbide		X	
95	Barium Carbonate	X		
96	Cyclohexylamine			X
97	Silver Nitrate	X		
98	Arsenic Compounds	X		
99	Ethyl Alcohol	X		
100	Acetone	X		

2. The chemicals react rapidly with liquid water or moisture or other components in air.

3. The compounds are strong acids or bases, or strong oxidizing reducing agents and may react with the components of the sealants.

The predictions for phosphorus and formaldehyde depend on the state of these chemicals. Red phosphorus probably can be sealed, while white phosphorus probably cannot be sealed. Formaldehyde as a monomeric gas has a normal boiling of -21 C, and would probably not be sealable because of its vapor pressure. In aqueous solution (37 percent) as formalin or in the polymeric forms of meta- or para-formaldehyde, it probably could be sealed by present methods.

PRELIMINARY DESIGN CONCEPTS

A number of preliminary design concepts were generated for consideration in application systems. These concepts are concerned with the broad range of leak situations likely to be encountered in practice. These include leaks in air and underwater, and different configurations such as round and elongated holes, cracks, open seams, leaking valves, and open pipes. When leaks occur underwater, the hydrostatic external pressure acts to reduce the net pressure behind the leak and makes leak sealing easier, compared to air.

Several concepts and ideas are described briefly in the remainder of this section. It should be noted that these are intended only to illustrate possibilities for using foams to seal various types of leaks. The emphasis is primarily on the applicator element; each concept would make use of similar systems (also to be developed in the future) for storing, feeding, and mixing the foam. Two concepts are illustrated for use in plugging irregularly shaped holes: the foam-filled balloon (Fig. 18) and the hollow rubber cone (Fig. 19). An approach to using a moving applicator head for plugging split seams and elongated openings is illustrated in Fig. 20; a variation of the hollow rubber cone idea might also be considered. The idea of using a foam cocoon or foam dome for sealing leaks from damaged valves or piping is illustrated in Fig. 21.

In the foam-filled balloon applicator (Fig. 18), an expandable rubber tube (or balloon) is attached securely to the end of a foam supply system. The end of the delivery tube with the balloon is pushed through the opening in the leaking container. The premixed foam components are injected into the balloon through the tube (both through the end and through selected circumferential holes). As the foam expands, the foam-filled balloon expands on both sides of the hole to form a mechanical bridge, and this securely holds the plug in place. The final foam density probably is not at all critical, i.e., a broad range of densities would be substantially equivalent in performance. Some advantages of this system are its simplicity and that the foam during its curing period is protected by the rubber tube, therefore eliminating any

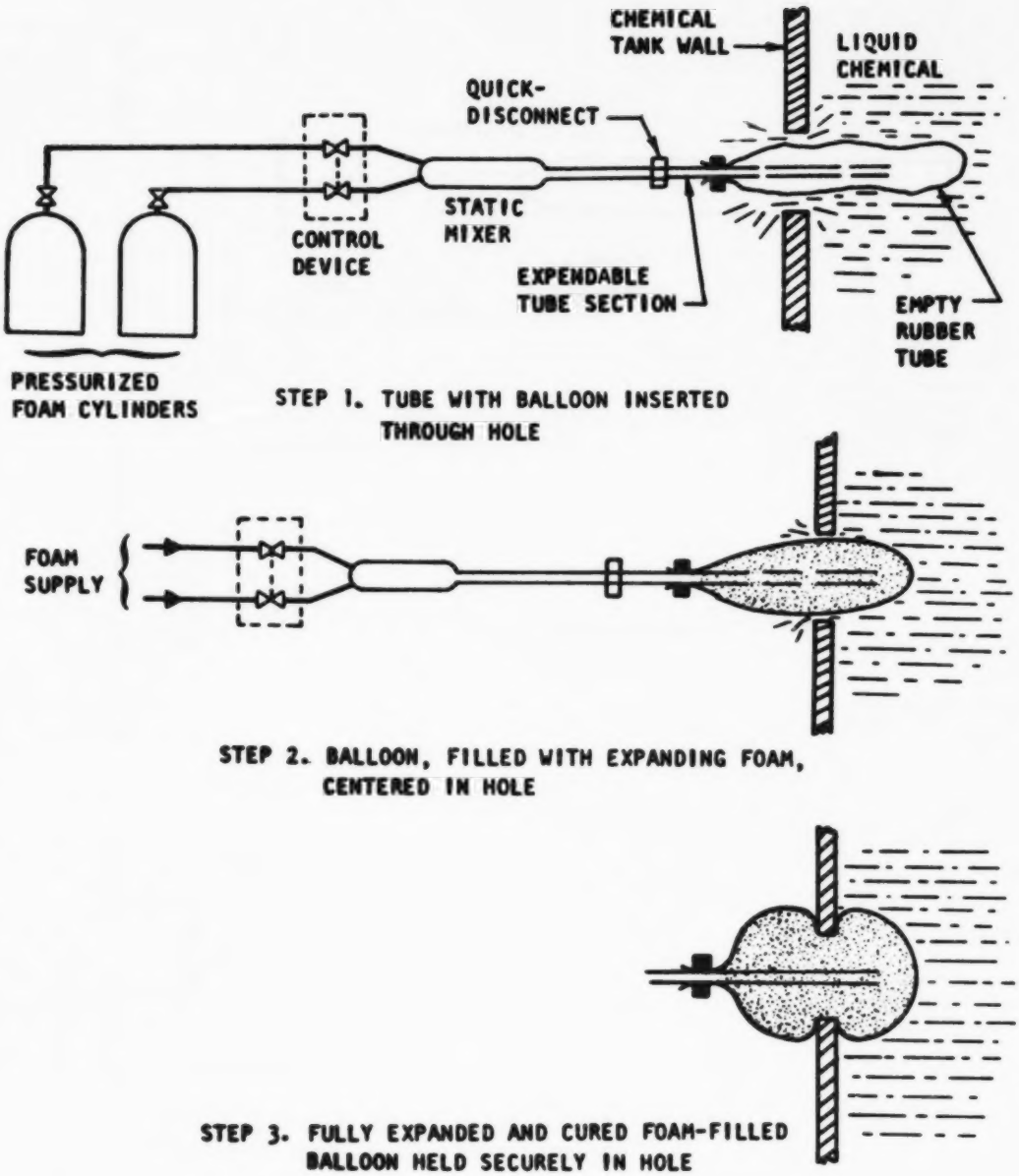

Figure 18. Foam-Filled Balloon Concept

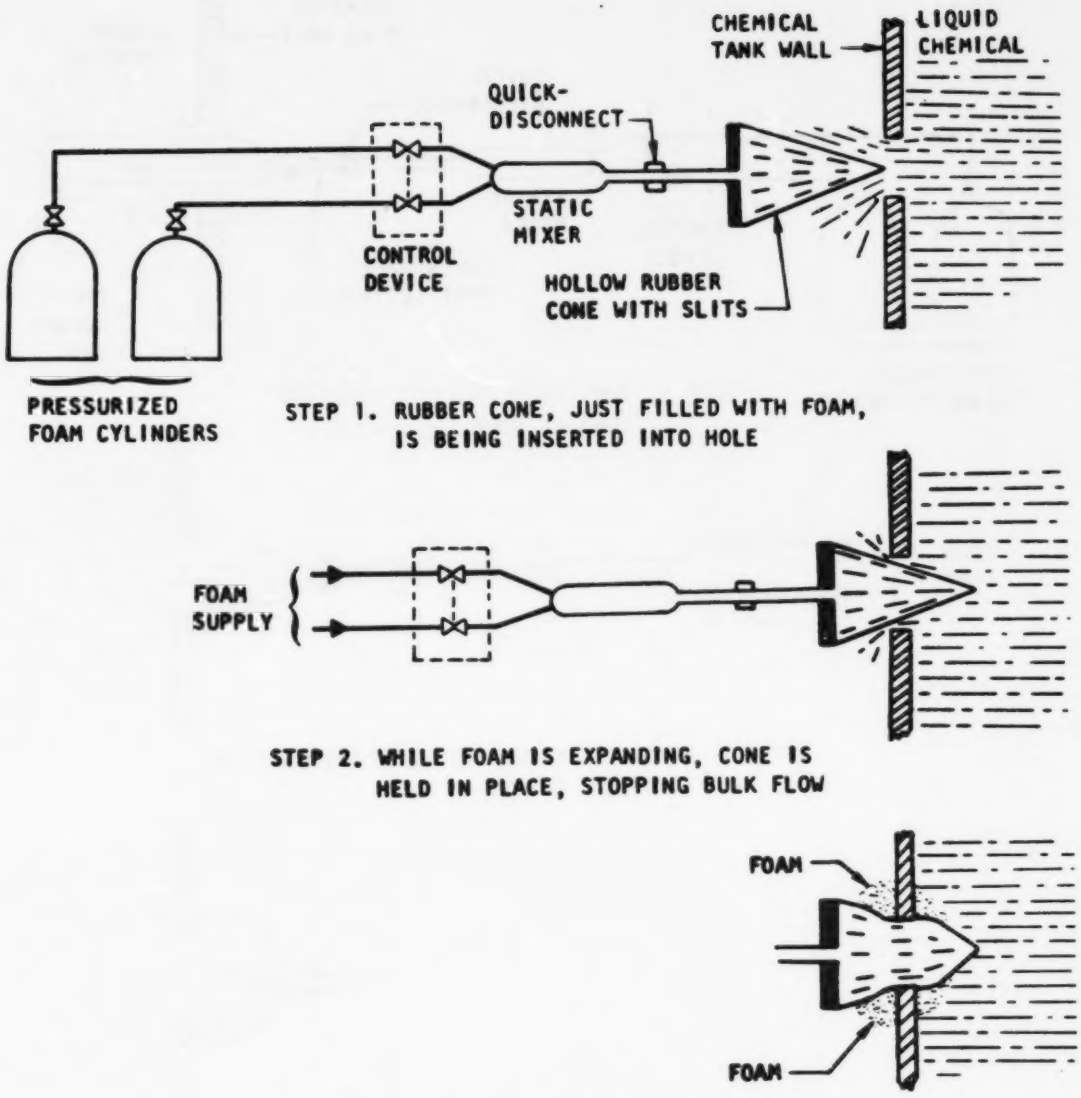
CHEMICAL TANK WALL
LIQUID CHEMICAL
QUICK-DISCONNECT
STATIC MIXER
CONTROL DEVICE
HOLLOW RUBBER CONE WITH SLITS
PRESSURIZED FOAM CYLINDERS
STEP 1. RUBBER CONE, JUST FILLED WITH FOAM, IS BEING INSERTED INTO HOLE
FOAM SUPPLY
STEP 2. WHILE FOAM IS EXPANDING, CONE IS HELD IN PLACE, STOPPING BULK FLOW
FOAM
FOAM
STEP 3. LEAK STOPPED; CURED FOAM AND SLIGHTLY EXPANDED CONE HOLDS CONE IN POSITION

Figure 19. Hollow Rubber Cone Concept

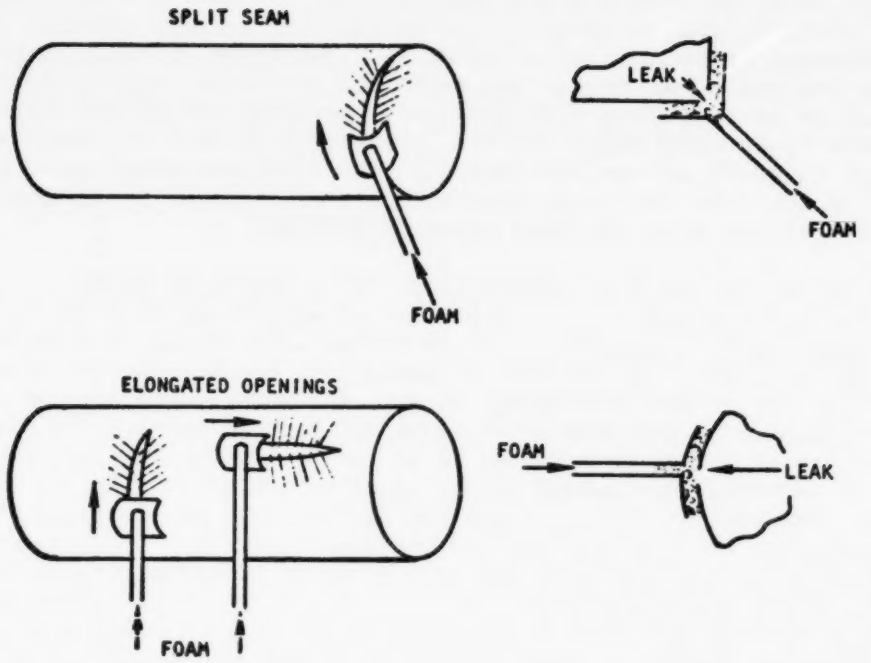

Figure 20. Moving Applicator Concepts

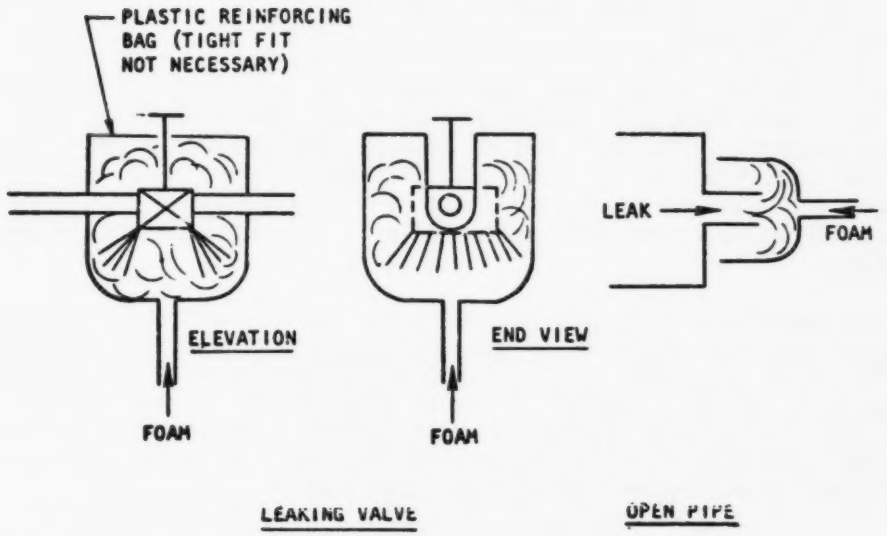

Figure 21. Foam Cocoon Concept for Leaking Valves and Open Pipes

possible reactions with the leaking chemical, and much of the erosive force of the fluid stream. A disadvantage is that the balloon prevents the foam from adhering to leaking container walls. Therefore, although bulk flow will be stopped, some seepage may exist and this will require additional application of foam for a complete seal. Although the balloon might be punctured by a jagged edge, the foam probably will have developed enough strength to avoid any serious leakage. The foam components could be included in the tube and pressurized with air or nitrogen to drive them through a static mixer and then into the balloon.

In the hollow rubber cone concept (Fig. 19) a semirigid rubber cone, with slits in it, is connected by its plastic or metal base to a tube or some other foam supply arrangement. It is filled with the mixed foam components, and then it is positioned or jammed into the hole in the chemical container. As in the preceeding concept, the rubber cone acts as a protective barrier to the foam as it is expanding and curing. The slight flexibility of rubber cone allows it to conform to some extent to the shape of an irregular opening in the chemical container. As the foam expands, the excess material comes out of the slits and fills in the remaining gaps between the cone and container opening. As opposed to the balloon concept, the foam can adhere to the container walls, thus forming a good leak-proof seal. With a cone of the proper rigidity, as the foam expands, the portion of the cone inside the container will expand slightly, helping to lock it in place. The foam would probably adhere to the rubber plug, if allowed to cure while in contact. This is desirable in the case of sealing a hole, but undesirable if this type of device were used to seal an elongated opening or seam. Each operational application system would probably need an assortment of different size cones; the choice of sizes would be based on a study of the tank failure modes most prevalent.

In both of the above concepts, the balloon or cone plug can be positioned on a long tube; this will afford the operator some protection from the leaking chemical. The tube can be used to transfer the foam components from small pressurized cylinders to the plugging device or applicator. The transfer tube and mixing tube can be discarded after use. The cost of a static mixing tube when produced in large quantities would be reasonable.

When the opening is long and narrow, as in split seams and elongated holes, the basic approach would be to use a moving applicator, as illustrated in Fig. 20. The applicator is rigid and would have various application heads contoured to follow a corner, a curved surface, or a plane surface. Because the openings are narrow, it is expected to be possible to seal by spraying foam directly into an opening; the application starts at one end of an opening and progresses to the other end.

A foam cocoon concept (Fig. 21) is envisaged for leaking valves or open (broken) pipes. A dome or reinforcing bag, with cutouts for piping where necessary, restricts the leak path and makes it possible for the foam to surround the leak completely (i.e., by forming a cocoon).

The preliminary design concepts presented illustrate some possible modes of using foams to seal various types of leaks in chemical containers. In developing a prototype system, the concept being considered would be broken down into its component parts (e.g., such as the applicator, foam supply system, etc.); then, each component part would require testing and development as necessary until it approaches or meets the desired requirements.

SECTION VI

ACKNOWLEDGEMENTS

The support of the project by the Environmental Protection Agency and the interest and involvement exhibited by the Project Officer, Ira Wilder, are acknowledged with sincere thanks.

This project was conducted in the Advanced Programs Department at Rocketdyne with Dr. B. L. Tuffly, as Program Manager, responsible for overall administration, and Dr. R. C. Mitchell, as Project Engineer, responsible for the technical content and conduct of the program. The other members of the project team were Drs. C. L. Hamermesh, M. Kirsch, J. E. Sinor, and Messrs. J. V. Lecce and J. J. Vrolyk. (This report has been assigned a Rocketdyne control number of R-9054.)

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SECTION VII

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2. Dawson, G. W., A. J. Shuckrow, and W. H. Swift, Control of Spillage of Hazardous Polluting Substances, Battelle Memorial Institute, Richland, Washington, FWQA Contract No. 14-12-866, November 1970.

3. R-8897, Methods to Control Hazardous Materials Spills, 16 mm color/silent film, Rocketdyne Division, Rockwell International, Canoga Park, California, March 1972.

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SECTION VIII

PUBLICATIONS AND PATENTS

Mitchell, R. C., M. Kirsch, C. L. Hamermesh, and J. E. Sinor, "Methods for Plugging Leaking Chemical Containers," Proceedings of the 1972 National Conference on Control of Hazardous Material Spills, Houston, Texas, 21-23 March 1972.

Several disclosures are being evaluated by the Rocketdyne Patents Department to decide whether to file patent applications.

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SECTION IX

GLOSSARY

A = cross-sectional area of fluid stream

A_c = cross-sectional area of container (in horizontal plane)

A_h = cross-sectional area of rupture, for flow

C = discharge coefficient = $C_c C_v$

C_c = contraction coefficient = $\frac{\text{area vena contracta}}{\text{area hole}}$

C_v = velocity coefficient = $\frac{u_2}{u_2^*}$

D_c = diameter of cylindrical container

e = geometry ratio of container = $\frac{H}{D_c}$

f = fractional liquid height after time T, i.e.,

$f = \frac{\text{height after time T}}{\text{original height}}$

g = local gravitational constant

g_c = conversion factor necessary to make Newton's Second Law dimensionally correct when using lbf and lbm $\left[= 32.174 \frac{\text{lbm-ft}}{\text{lbf-sec}^2}\right]$

H = length of cylindrical container

h = effective liquid head above rupture opening

p = local pressure

Q = volumetric flowrate

T = time required for liquid level to drop to some fraction (f) of H

u = local velocity (any effects of nonuniform velocity distributions neglected for these purposes)

u^* = local velocity for ideal fluid

V = volume of container = $\pi D_c^2 H/4$

Z = elevation of specified station (referenced to any consistent datum)

ρ = fluid density

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APPENDIX

DERIVATION OF EQUATIONS FOR ENVELOPE OF PRACTICAL APPLICATIONS

Derivations are given in this section for the equations used in Section V to define an approximate envelope of practical applicability of methods for stopping leaks in chemical containers. The symbols are defined in the Glossary.

BASIC CONSIDERATIONS

The region of application is considered to be limited by two factors:

1. Time for response (If the rupture is too large, there will not be enough time to respond.)
2. Limits of human strength (The limiting constraint is taken as the hydraulic force of the fluid stream, which will be transmitted to the leak-sealing device, assumed to be portable and operated by one man.)

THE SYSTEM

A cylindrical tank of diameter D_c, height H, and volume V ($= \pi D_c^2 H/4$) is considered. An opening of characteristic diameter D is located at depth h below the free surface of the liquid in the container, as shown in Fig. 22 for containers at different attitudes.

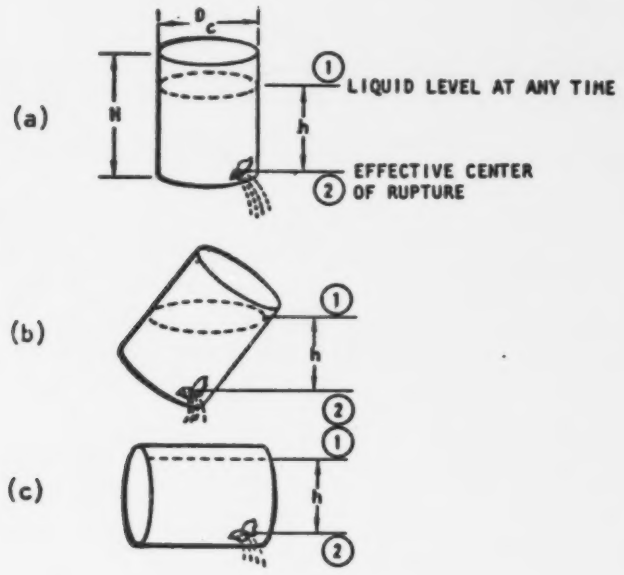

Figure 22. Sketch of Basic Container in Different Attitudes

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TIME FOR RESPONSE

If we apply the Mechanical Energy form of Bernoulli's Theorem to a ruptured container between station 1 (free liquid surface) and station 2 (at the vena contracta of the stream gushing from the rupture) (see Fig. 22):

$$(Z_1-Z_2)\frac{g}{g_c} + \frac{u_1^{*2}-u_2^{*2}}{2g_c} + \frac{p_1-p_2}{\rho} = 0 \qquad (4)$$

where

$Z_1-Z_2 = h$ by definition

$u_1^{*2} << u_2^{*2}$ and can be neglected

$p_1 = p_2$ (We are not considering pressurized tanks in this case.)

Equation 1 reduces to

$$u_2^{*} = \sqrt{2gh} \qquad (5)$$

Equation 2 gives a simple expression for the velocity of an ideal fluid discharging from a container (neglecting friction effects). In reality, frictional effects will keep the actual velocity of the discharge stream below the value given by Eq. 5. Introducing a velocity coefficient, C_v,

$$u_2 = C_v\sqrt{2gh} \qquad (6)$$

Applying the Equation of Continuity and introducing a contraction coefficient, C_v (to account for the vena contracta effect), converts Eq. 6 into:

$$Q = u_2 A_2 = u_2 A_h C_c = C_c C_v A_h \sqrt{2gh} \qquad (7)$$

or

$$Q = C A_h \sqrt{2gh} \qquad (8)$$

Now, we want to use this result to develop an expression for the time required for the liquid level in the container to drop by a specific amount

$$\frac{dh}{dt} = -\frac{Q}{A_c} \qquad (9)$$

Q is a function of h (Eq. 8) and, in the general case, A_c will also be a function of h (specific for a given container geometry and attitude)

$$\int_{t_a}^{t_b} dt = - \int_{h_a}^{h_b} \frac{A_c(h)}{Q(h)}\, dh \tag{10}$$

To proceed further, it is necessary to specify $A_c(h)$. Taking the simple case of a cylindrical tank with its axis vertical (Fig. 22(a)):

$$A_c = \pi D_c^2/4$$

Using this and Eq. 8 in Eq. 10, plus specific limits which assume the worst case (shortest time available) of starting with the container full of liquid and the rupture at the bottom (h = H),

$$\int_0^T dt = - \int_H^{fH} \frac{\pi D_c^2}{4CA_h\sqrt{2gh}}\, dh$$

$$T = \frac{2}{C}\left(\frac{D_c}{D}\right)^2 \left(\frac{H}{2g}\right)^{1/2} (1 - f^{1/2}) \tag{11}$$

Introducing $e = H/D_c$ and $V = \pi D_c^2 H/4$, and thereby eliminating H and D_c, yields

$$T = 2\left(\frac{4}{\pi}\right)^{5/6} (1 - f^{1/2}) \frac{V^{5/6}}{C D^2 e^{1/3} (2g)^{1/2}} \tag{12}$$

$$T = \frac{0.3049\ (1 - f^{1/2})\ V^{5/6}}{C D^2 e^{1/3}} \tag{13a}$$

with T in seconds, V in ft^3, and D in feet (C, e, and f are dimensionless).

If it is desired to express Eq. 13a with V in gallons and D in inches, the constant is changed:

$$T = \frac{8.209\ (1 - f^{1/2})\ V^{5/6}}{C D^2 e^{1/3}} \tag{13b}$$

which is given as Eq. 1 in Section V of this report. Typical values for a sharp-edged (not countoured) hole are $C_c \simeq 0.62$, $C_v \simeq 0.98$, $C \simeq 0.61$.

If we take as a criterion of maximum allowable flow (minimum allowable response time),

$$f = 0.70 \text{ in } T = 120 \text{ seconds}$$

Then Eq. 10b becomes

$$D = 0.1353\ V^{5/12}/e^{1/6} \quad (V \text{ in gallons, } D \text{ in inches}) \tag{14}$$

which is given as Eq. 2 in Section V of this report.

Numerical results for several values of e are:

e	$D/V^{5/12}$
0.25	0.170
0.5	0.152
1.0	0.135
1.5	0.1265
2.0	0.121
3.0	0.113
4.0	0.107

This range of values of e covers essentially any practical situation, e.g., $e \simeq 2$ to 4 would be typical of a truck or railway tanker upended to sit vertically; $e \simeq 1.5$ to 2 is typical of chemical drums; and $e \simeq 0.25$ to 0.5 would represent truck or railway tankers in a normal (horizontal axis) orientation. Strictly speaking, one would need to change the $A_c(h)$ function in Eq. 10 and derive a correspondingly changed Eq. 14 for any tank orientation other than a vertical cylinder (Fig. 22(a)), with slightly changed numerical constants in the tabulation above.

Because of the 1/6 power of e in Eq. 14, D is relatively insensitive to changes in e. For present purposes (to provide a perspective for thinking about sizes of ruptures to be plugged), one may use a single value of e, e.g., e = 1.5, so that Eq. 14 becomes

$$D = 0.1265\ V^{5/12} \tag{15}$$

LIMIT OF HUMAN STRENGTH

The force required to counteract the hydraulic pressure is

$$F = A_h\ h\ \rho\ \frac{g}{gc} \tag{16}$$

If we take, for a representative case, h = H (i.e., a full tank), with $A_h = \pi D^2/4$, and $V = \pi D_c^2 H/4 = \pi H^3/4 e^2$, Eq. 16 becomes:

$$F = \frac{\pi}{4}\left(\frac{4e^2V}{\pi}\right)^{1/3} \rho \frac{g}{gc}$$

Cubing both sides and rearranging:

$$VD^6 = \frac{16 F^3}{\pi^2 e^2 \left(\rho \frac{g}{gc}\right)^3} \tag{17}$$

with V in cu ft, D in feet, ρ in lbm/cu ft, and F in lbf. This equation is given in Section V as Eq. 3.

COMPARISON OF FORCES REQUIRED TO OVERCOME HYDRAULIC PRESSURE AND FLUID MOMENTUM

The force required to overcome the static pressure from a fluid height h with a hole of area A_h is

$$F_p = \rho \frac{g}{gc} h A_h \tag{18}$$

The maximum force required to overcome the momentum of a gushing fluid stream escaping from a hole is obtained by assuming that: (1) the stream is being deflected at the vena contracta (i.e., point of maximum velocity), (2) the total momentum of the stream is imparted to the applicator. For these assumptions, the impulse-momentum principle gives the following equation for the force required to overcome the stream momentum:

$$F_m = \frac{Q \rho u_2}{gc} \tag{19}$$

where u_2 is the mean velocity at the vena contracta. Eliminating u_2 and Q by the use of Eq. 8 and 10 gives:

$$F_m = 2 C_c C_v^2 \rho \frac{g}{gc} h A_h \tag{20}$$

Comparison of Eq. 18 and 20 gives:

$$\frac{F_m}{F_p} = 2 C_c C_v^2 \tag{21}$$

Using typical values for a sharp-edged circular hole ($C_c = 0.62$, $C_v = 0.98$) produces the result

$$\frac{F_m}{F_p} \simeq 1.20$$

which means that the force required to overcome the momentum of the liquid stream could be as much as 20 percent greater than that necessary to overcome the static pressure developed by blocking the same opening. It may be possible to reduce F_m substantially by clever design of the applicator head to cause appropriate deflection of the fluid stream as the applicator is moved into position. For this reason, it was decided to use the definable value of F_p as the requirement on human strength.